Resolving the Full Picture: Complementary Spectroscopic Approaches to Explore Dynamics in Physical and Chemical Systems

714. WE-Heraeus-Seminar

16 – 19 February 2020
Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de.

Scope of the 714. WE-Heraeus-Seminar:

This seminar will cover time-resolved spectroscopic methods to investigate dynamic systems in the interdisciplinary field of physics, chemistry, biology, materials- und life-sciences. The timescales of dynamic processes occur over many orders of magnitude from atto- and femtoseconds to days. Examples are light-induced excitation, cooling and separation of charge carriers in photovoltaics (fs to ps), complex kinetics of chemical catalysis as well as the structure-function relationship in (photo)chemical and biochemical systems (ns to µs) and the chemical degradation of catalysts (µs to days). These examples are united by the fact that inherent dynamic processes span several orders of magnitude in time and only their overall sum allows for entirely understanding the properties of a system. There is a large number of spectroscopic and specialized analysis methods for the above-mentioned processes that require a high degree of expertise. We expect a significant gain if these methods can be combined to completely cover the description of a system.

We strive to broaden the understanding of time-resolved methods and connect researchers on specific methods and systems by discussing current scientific questions from different perspectives. The individual topics will be introduced by experts, spectroscopists and method developers, followed by presentations of the participants in order to promote new collaborations and enable efficient networking.

We will set a special focus on young academics who often have to face the challenge to become independent experts in a narrow field, but also need to review their work critically in light of the full picture of their research.

Scientific Organizers:

Dr. Klaus Boldt	Universität Konstanz / Germany E-mail klaus.boldt@uni-konstanz.de
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Introduction

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Registration:

Jutta Lang (WE-Heraeus Foundation)
at the Physikzentrum, reception office
Sunday (17:00 h – 21:00 h) and
Monday morning

Door Code:

(Key symbol button) 2 7 1 4 #

For entering the Physikzentrum
during the whole seminar

Program

Program

Sunday, 16 February 2020

17:00 – 21:00	Registration	
from 18:30	*BUFFET SUPPER / Informal get together*	

Monday, 17 February 2020

07:30	*BREAKFAST*	
08.15 – 08:25	Scientific organizers	**Opening and welcome Introductory notes**

Pico- to Nanoseconds: Transient States

08:30 – 09:30	Oliver Wenger	**Electron transfer dynamics and photophysical processes in metal complexes monitored by one- and two-pulse laser flash photolysis**
09:30 – 09:45	Jens Uhlig	**Ultrafast electron dynamics in real world light activated complexes studied by x-ray spectroscopy**
09:45 – 10:00	Kristoffer Thom	**Characterisation of OLED emitters: A challenge for time-resolved spectroscopy**
10:00 – 10:30	*COFFEE BREAK*	
10:30 – 11:30	Benjamin Dietzek	**Excited-state processes in catalytically competent intermediates of a molecular photocatalyst**
11:30 – 11:45	Joachim Kübel	**Pump-20*probe – making the best of different repetition rates**

Program

Monday, 17 February 2020

11:45 – 12:00	Pavel Malý	**Interplay of slow protein and ultrafast electronic dynamics in photosynthesis: A case for ultrafast single-molecule spectroscopy**
12:00 – 12:15	Christian Wiebeler	**Simulation of ultrafast photoinduced processes in organic molecular systems**
12:15	**Conference Photo** (in front of the lecture hall)	
12:20	*LUNCH*	

Nano- to Microseconds: Intermediates

13:45 – 14:45	Angelika Brückner	**Monitoring charge separation and transfer in photocatalysis by in situ EPR spectroscopy**
14:45 – 15:30	**Discussion forum**	
15:30 – 17:30	**Poster session I**	(with *COFFEE*)
17:30 – 17:45	Alexander Schubert	**Charge generation via hole transfer in fullerene-based bulk heterojunction solar cells – A first-principles rate-theory approach complementing recent multispectral 2DES experiments**
17:45 – 18:00	Lea Ress	**Accessing chiral dynamics via broadband time-resolved circular dichroism spectroscopy**
18:00 – 18:15	Muslim Dvoyashkin	**Potential of the pulsed field gradient NMR for direct probing of the ionic dynamics in materials for supercapacitors**
18:15 – 18:30	Stefan Jorda	**About the Wilhelm and Else Heraeus-Foundation**
18:30	*HEREAUS DINNER at the Physikzentrum* *(cold & warm buffet, free beverages)*	
20:30	**Get together and "Ask the Prof"**	

Program

Tuesday, 18 Feburary 2020

07:30	*BREAKFAST*	

Femto- to Picoseconds I: Coherences and 2D Spectroscopy

08:30 – 09:30	Alfred Leitenstorfer	**Electronic systems under elementary spatio-temporal confinement**
09:30 – 09:45	Ryan Crisp	**Combining different spectroscopies to quantify the flow of electrons in quantum dot films**
09:45 – 10:00	Christine Schedel	**Time-resolved photocurrent measurements**
10:00 – 10:30	*COFFEE BREAK*	
10:30 – 11:30	Giulio Cerullo	**Broadband two-dimensional electronic spectroscopy with a birefringent interferometer**
11:30 – 11:45	Johann Mattiat	**Simulation of optical spectra in the time-domain**
11:45 – 12:00	Christoph Merschjann	**Semiconductor, insulator, or molecule – do we understand excitation and transport in "graphitic carbon nitride"?**
12:00 – 12:15	Jenny Schneider	**Electron transfer reorganization energies in the electrode-electrolyte double layer**
12:15	*LUNCH*	

Tuesday, 18 June 2019

Femto- to Picoseconds II: Coherences

13:45 – 14:45	Ulrike Woggon	**Coherent spectroscopy of near-infrared materials**
14:45 – 15:30	**Discussion forum**	
15:30 – 17:30	**Poster session II**	(with *COFFEE*)
17:30 – 17:45	Yang Ran	**Two-beam ultrabroadband coherent anti-stokes raman scattering spectroscopy for temperature and concentration measurements using a dual-output OPCPA**
17:45 – 18:00	Josef Tiggesbäumker	**Strong laser field induced Coulomb explosion of clusters and droplets: Exploring the dynamics from atto- to microseconds**
18:00 – 18:15	Jan Christoph Thiele	**Macromolecular diffusion dynamics on the nanometre scale studied with MIET**
19:00	*DINNER*	
20:30	Ursula Keller	**Attosecond science: Opportunities and challenges for measurements at the limit**

Program

Wednesday, 19 February 2020

07:30	*BREAKFAST*	

Far-IR Spectroscopy

08:30 – 09:30	Melanie Schnell	**Deciphering the structure, dynamics, and chirality of complex molecules**
09:30 – 09:45	Rowan MacQueen	**Triplet fusion photon upconversion: at the intersection of photonics and photochemistry**
09:45 – 10:00	Henrike Müller-Werkmeister	**Time-resolved serial crystallography: watching proteins in action from femtoseconds to seconds**
10:00 – 10:30	*COFFEE BREAK*	
11:30 – 11:30	Laurens Siebbeles	**Excitons are stable in ultrathin CdSe nanoplatelets: Even at high density!**
11:30 – 11:45	Scientific organizers	**Poster awards and closing remarks**
12:00	*LUNCH*	

End of the seminar *and FAREWELL COFFEE* ***/ Departure***

Posters

Posters

1.	Daniel Becker	**Time dependent IR induced action spectroscopy of sodium doped water clusters**
2.	Sebastian Bold	**Transient absorption spectroelectrochemistry on dye-sensitized photocathodes**
3.	Avinash Chettri	**It takes three to tango-Investigating the excited state properties of TLD-1433 family with increasing thiophene chain length**
4.	Florian Döttinger	**Tailored phenanthroline-based ligands for heteroleptic copper(I) photosensitizers**
5.	Danja Fischli	**Anisotropic nanocrystal growth from local monomer hotspots**
6.	Marco Flock	**A ps time-resolved photoelectron imaging study on the photophysics of tolane**
7.	Jer-Shing Huang	**Direct observation of negative Goos-Hänchen shift and plasmon coupling in self-assembled semiconducting polymer microspheres on a plasmonic substrate**
8.	Lars Klepzig	**Lead chalcogenide nanoplatelets and their optoelectronic properties**
9.	Christian Klinke	**Synthesis and optoelectronic properties of two-dimensional colloidal nanomaterials**
10.	Bennet Krebs	**Angular resolved photoemission of metal atoms embedded in helium nanodroplets in the MPI regime**
11.	Sonja Krohn	**Monitoring the growth of CdSe/CdS giant-shelled nanocrystals by spectroscopic measurements**
12.	Stephan Kupfer	**Towards unidirectional multi-electron transfer processes in photocatalysis – A theory-driven design**
13.	Roman Kusterer	**Real-time monitoring of photoinduced processes on semiconducting nanowires in various chemical environments**
14.	Julian Lüttig	**Direct comparison of fluorescence-detected and coherently detected high-order two-dimensional spectroscopy**

Posters

15.	Monalisa Mallick	**Towards time-resolved study of two-dimensional semiconductor nanomaterials using extreme ultraviolet spectroscopy**
16.	Mathias Micheel	**Molecular functionalization of inorganic semiconductor nanostructures**
17.	Samuel Monter	**Growth mechanism and electronic properties of tipped nanorods**
18.	Stefan Müller	**Resolving electronic structure systematically by coherent multiple-quantum multidimensional fluorescence spectroscopy**
19.	Djawed Nauroozi	**N-Doped nanographene as ligand in metal complexes**
20.	André Niebur	**Theoretical studies of edge states in transition metal dichalcogenide monolayers and nano-platelet preparation by colloidal synthesis**
21.	Jens Niederhausen	**Triplet exciton dynamics at silicon-organic interfaces**
22.	Heshmat Noei	**Time resolved photoemission study of the charge transfer dynamics in anatase TiO_2 for CO photooxidation to CO_2**
23.	Yannik Pfeifer	**Investigation of photolabile protection groups as tools for time-resolved structural dynamics**
24.	Jannik Rebmann	**Synthesis and bandgap engineering of anisotropic ZnSe/CdS heterostructured colloidal nanoparticles**
25.	Marina Rosebrock	**Mixed semiconductor and noble metal nanoparticle gel-networks**
26.	Nils Rosemann	**Separated and recombined again – Tracking ultrafast bimolecular charge transfer in iron-sensitizer based systems**
27.	Eva Schaefer	**A kinetic insight in the linear oriented assembly and attachment of au-nanoparticles towards 1D structures**
28.	Marcus Scheele	**Structure-transport correlations in nanocrystal superlattices**

Posters

29.	Marie-Ann Schmid	**Excited states of Ru(II) and Cu(I) photosensitizers with dipyrido-phenazine/ naphto-phenanthroline derivates as ligands**
30.	Michael Seybold	**Influence of CdSe intermediates on nanocrystal shape**
31.	Selflando Shehaj	**Proton transport properties of SO^3- groups in Ionic Liquids (IL), studied by vbrational spectroscopy**
32.	Denis Tikhonov	**Generating and probing molecular chirality in the gas phase**
33.	Cheng-Jui Tso	**Roaming dynamics and conformational memory in photolysis of formic acid at 193 nm using time-resolved fourier-transform infrared emission spectroscopy**
34.	Andreas Volkmer	**Time-resolved ultrafast spectroscopies performed under tight focusing conditions**
35.	Hans Werners	**Fluorescence spectral diffusion of single type-II semiconductor ZnSe/CdS dot-in-rod nanostructures at room and cryogenic temperatures**
36.	Yingya Yang	**The impact of a fused naphthaloylenebenzene moiety at 1,10-phenanthroline on the electron storage capability and the spectroscopic characterization of the Cu(I) and Ru(II) photosensitizers**
37.	Michael Zabel	**Temporal development of a laser-induced helium nanoplasma measured through auger emission and above-threshold ionization**
38.	Xiaodong Zhao	**N_2^+-lasing induced by filamentation in air for femtosecond coherent anti-stokes Raman spectroscopy**

Abstracts of Lectures

(in chronological order)

Electron Transfer Dynamics and Photophysical Processes in Metal Complexes Monitored by One- and Two-Pulse Laser Flash Photolysis

L. A. Büldt[1], F. Glaser[1], P. Herr[1], X. Guo[1], P. Hamm[2], C. Kerzig[1], M. Kuss-Petermann,[1] C. B. Larsen, S. Neumann[1], J. Nomrowski[1], M. Orazietti[2], A. Pannwitz[1] and O. S. Wenger[1]

[1]*Department of Chemistry, University of Basel, Switzerland*
[2]*Department of Chemistry, University of Zurich, Switzerland*

The first part of this talk focuses on the application of laser flash photolysis for investigations of photoinduced electron transfer in donor-sensitizer-acceptor compounds. Of key interest are light-driven multi-electron transfer reactions leading to charge accumulation as well as proton-coupled electron transfer, because these processes are important for artificial photosynthesis. The use of transient infrared spectroscopy as a tool for distinguishing between different photochemical products will be illustrated.

The second part of the talk will concentrate on the application of two-pulse two-color laser flash photolysis (or pump-pump-probe spectroscopy) for the generation of hydrated electrons as super-reductants for photoredox catalysis.

In the last part of the talk, the usefulness of time-resolved emission and transient UV-Vis spectroscopy for investigations of new photoactive metal complexes made from Earth-abundant elements will be discussed.

Ultrafast electron dynamics in real world light activated complexes studied by x-ray spectroscopy.

J. Uhlig et al.

Chemical Physics, Lund University, Lund, Sweden

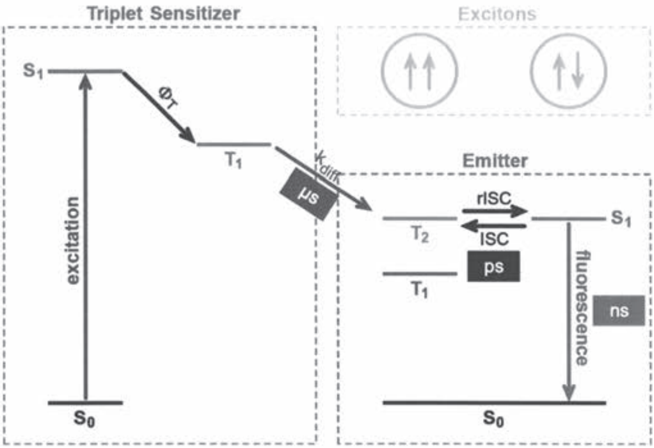
With the recent advances in the development, performance and availability of ultra-short x-rays pulses it has become possible to use element selective spectroscopy as a regular tool in sample characterization. In the field of light sensitization and light activated catalysis these tools are increasingly used to study model complexes and learn the principles behind the observed dynamics. Understanding these principles in turn has led to the development of extraordinary new complexes capable of harvesting and using solar energy. During recent years the experimental conditions have improved and now allow the study of realistic complexes that are active as catalysts and/or drive light harvesting in dye sensitized solar cells. We will show a number of examples in which we used x-ray spectroscopy to understand the light induced dynamics in complex molecular systems. First a series of iron carbene sensitizers that allow the construction of dye sensitized solar cells based on earth abundant materials. We will discuss the electronic and vibrational dynamics studied with x-ray emission spectroscopy and x-ray scattering including some hot electron dynamics critical for future applications. Secondly we discuss the dynamics at the catalytic reaction center of several light activated hydrogen evolving Ru-Pt catalysts studied with XAS at the reaction center. We found beside the expected electron transfer clear evidence for a chemical reaction triggered by light that consumed two electrons after the activation with a single absorbed photon and thus a potential pathway to avoid the usual requirement of multi photon processes for hydrogenase in molecular systems. We will finish by presenting a series of table top systems producing ultrafast pulses of x-rays from a laser between 1mJ and 100mJ now enabling groups to perform similar measurements in the laboratory.

Characterisation of OLED Emitters: A challenge for time-resolved spectroscopy

K. Thom[1] and P. Gilch[1]

[1] *Institute for Physical Chemistry II, Heinrich Heine University, Düsseldorf, Germany*

Organic light-emitting diodes (OLEDs) become more and more important as efficient alternatives as light sources, especially in displays. In OLEDs molecular emitters are excited by electron-hole pair recombination. From that singlet and triplet excitations result. The decay of these excitations and their interconversion can occur on time scales ranging from femto- to microseconds. The combination of different time-resolved absorption and emission techniques can yield a comprehensive picture of the photophysics of OLED emitters. This is demonstrated relying on our studies on aromatic carbonyls. [1,2] They constitute a very promising new type of OLED emitters utilizing high reverse intersystem crossing (rISC) to generate light.



In different absorption and fluorescence experiments a triplet sensitizer (serving as a stand-in for triplet excitons) is optically excited. Its energy can be transferred by a diffusional process towards the emitter, which finally emits fluorescence light. The ongoing processes span over several orders of magnitude in time as well as signal intensity. [3]

References

[1] T. Villnow, J. Phys. Chem A **118**, 11696 (2014)
[2] C. Torres Ziegenbein, ChemPhysChem **18**, 2314 (2017)
[3] K. Thom, q&more, July 17, 2019

Excited-State Processes in Catalytically Competent Intermediates of a Molecular Photocatalyst

Benjamin Dietzek

[1]Department Functional Interfaces, Leibniz Institute of Photonic Technology Jena
[2] Institute of Physical Chemistry, Friedrich Schiller University Jena

Hetero-bimetallic complexes constitute versatile model systems to study intermolecular energy and electron transfer reactions. Furthermore, they present attractive stepping stones in adapting the concepts of natural photosynthesis to man-made-systems, i.e. "artificial photosynthesis". In this presentation ultrafast photophysics in a transition metal complex molecular photocatalyst will be discussed, which constitutes (by now) a well-studied model systems for photodriven charge transfer. The talk will elude on novel spectroscopic approaches to study the excited states of intermediates in the charge-transfer cascades, which form the mechanistic basis for photocatalytic hydrogen production using the hetero-bimetallic complexes as photocatalysts.

References

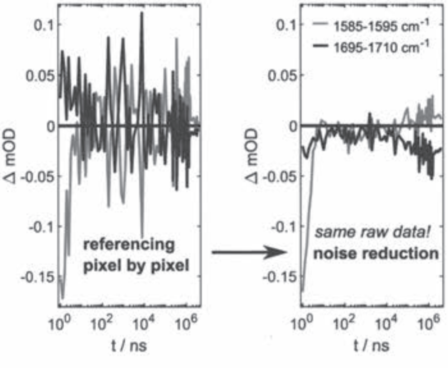
[1] L. Zedler et al., Angewandte Chemie International Edition (2019)
[2] S. Tschierlei et al., Chemistry – European Journal (2009)
[3] S. Bold et al., Chemical Communications (2018)
[4] L. Zedler et al., Chemical Communications (2014)
[5] M. Pfeffer et al., Angewandte Chemie International Edition (2015)
[6] M. Wächtler et al., Chemistry – European Journal (2015)

Pump-20*probe – making the best of different repetition rates

J. Kübel, **S. Westenhoff and M. Maj**

Department of Chemistry and Molecular Biology, 40530, Gothenburg, Sweden

The analysis and interpretation of time-resolved spectroscopic data is challenging in the presence of high levels of noise. Frequently, the obvious experimental route to desired spectroscopic information is simply not possible as the noise dominates the measured signal. Here, we extend the application of the noise reduction algorithm developed for heterodyne spectroscopy by Ge and co-workers.[1,2] We demonstrate that the application of such noise reduction scheme makes it possible to study transient absorption of very low quantum yield photochemical processes and low concentration samples. The proposed scheme improves data quality considerably and allows for extracting additional spectroscopic information that is otherwise inaccessible due to very low signal-to-noise ratio. We apply the new approach to monitor the complete Pr-to-Pfr transition in the Y263F mutant of the bacterial phytochrome of Deinococcus Radiodurans covering six orders of magnitude, from nanoseconds to milliseconds, in the mid-infrared. Our data demonstrates the versatility and usefulness of the noise reduction scheme.



References

[1] Y. Feng, I. Vinogradov and N.-H. Ge, Opt. Express **25**, 26262 (2017)
[2] Y. Feng, I. Vinogradov and N.-H. Ge, Opt. Express **27**, 20323 (2019)

Interplay of slow protein and ultrafast electronic dynamics in photosynthesis: A case for ultrafast single-molecule spectroscopy

P. Malý[1]

[1] *Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Germany*

The primary processes of photosynthesis have almost unity quantum efficiency thanks to the ultrafast speed of the excitation energy transfer and charge separation. These take place in delicately built antenna and reaction center pigment-protein complexes. While the pigments interact with light, the protein acts as a dynamic scaffold, determining the pigment properties. The slow protein conformational changes thus dynamically control the ultrafast light-harvesting function. In order to understand the function of the complexes, their dynamics across timescales has to be followed.

In our work we connect the slow and ultrafast dynamics by combining nonlinear and single-molecule spectroscopy. The single-molecule approach enables us to track the fluctuations of individual proteins, while employing ultrafast laser pulses provides the necessary time resolution.

One option how to connect the two spectroscopy realms is building a microscopic, excitonic model, which describes simultaneously several steady-state and time-resolved ensemble spectra, together with the single-molecule spectroscopy data[1]. In my contribution I will focus on a second approach, where we directly combine the techniques themselves. We thus develop ultrafast, nonlinear, fluorescence-detected single-molecule spectroscopy. First in an incoherent variant, which we demonstrate on the LH2 antennas of purple bacteria[2], and second in a coherent variant analogous to pump-probe. These techniques enable to directly observe how the slow protein dynamics alter the ultrafast energy transfer.

References

[1] P. Malý, A. T. Gardiner, R. J. Cogdell, R. van Grondelle, T. Mančal, Phys. Chem. Chem. Phys. **20**, 4360 (2018)

[2] P. Malý, J. M. Gruber, R. J. Cogdell, T. Mančal, R. van Grondelle, Proc. Natl. Acad. Sci. U.S.A. **113**, 2934 (2016)

Simulation of ultrafast photoinduced processes in organic molecular systems

C. Wiebeler[1]

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Computational simulations can be employed to aid in the interpretation of ultrafast spectroscopy by giving molecular insights into photoinduced processes. Nonadiabatic ab initio molecular dynamics based on Trajectory Surface Hopping (TSH) is an efficient approach to achieve this. It can be employed to investigate a diverse set of ultrafast photophysical and/or photochemical processes.

In the first part, we elucidate the dynamics of the photochemical cycloreversion reaction of diarylethenes (DAE). These simulations confirm and give insights into the difference in quantum yields for this reaction between two prototypical molecules [1]. Also the quantum yields and reaction times of an experimentally relevant DAE are described correctly [2].

In the second part, we discuss our more recent findings on ultrafast excitation energy transfer in an orthogonal molecular dyad composed of tetrathiophene (T4) and boron-dipyrromethene (BODIPY). In accordance with experiments, we observe that the excitation is first localized on T4, but is transferred within 100 fs to BODIPY [3].

In our efforts to model ultrafast photoinduced processes in systems of increasing complexity, we are now investigating organic chromophores inside proteins. In our initial study we could elucidate the difference in absorption between two forms of a photochromic protein via quantum mechanics/molecular mechanics (QM/MM) [4]. Next, we plan to investigate the photochemistry of the phycocyanobilin (PCB) chromophore inside this protein and in solution. This will allow us to better understand the influence the protein exerts on the PCB photochemistry.

References

[1] C. Wiebeler and S. Schumacher, J. Phys. Chem. A **118**, 7816–7823 (2014)
[2] C. Wiebeler *et al.*, Phys. Chem. Chem. Phys. **16**, 14531–14538 (2014)
[3] C. Wiebeler *et al.*, J. Phys. Chem. Lett. **8**, 1086–1092 (2017)
[4] C. Wiebeler *et al.*, Angew. Chemie Int. Ed. **58**, 1934–1938 (2019)

Monitoring charge separation and transfer in photocatalysis by in situ EPR spectroscopy

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For rational design of highly effective photocatalysts beyond the still dominating approaches of trial and error, the properties for optimum charge separation and transfer must be known. This requires the use of suitable spectroscopic in situ techniques, among which electron paramagnetic resonance (EPR) is particularly useful since it can directly visualize unpaired electrons, e. g. when they are trapped at different positions in semiconductors or in radicals formed from different substrates. Opportunities and limitations of in situ EPR spectroscopy for mechanistic studies in photocatalysis with semiconductors will be illustrated by three examples:

Example I comprises abatement of organic pollutants in water by nano-structured C_3N_4 with visible light [1]. In situ EPR coupled with spin trapping has been used to monitor photoexcitation of electrons, their capture by dissolved O_2 and O_3 to form $^\bullet OH$ and $^\bullet O_2^-$ radicals and the role of the latter in the photocatalytic mechanism. A new semiquantitative concept is presented, that links the band structure of the photocatalyst with the yield of radicals and the degradation rate of organic pollutants using the number of reactive charge carriers as a common descriptor.

In Example II, mesoporous $AgIn_5S_8/C_3N_4$ and MoS_2/C_3N_4 composites with surface Pt nanoparticles as cocatalyst have been monitored by in situ EPR during photocatalytic H_2 evolution from water. Catalyst stability was raised when a thin layer of the sulfide covers the C_3N_4 surface. While the sulfides themselves where not able to produce photoelectrons active for proton reduction, they promoted their transfer from the C_3N_4 conduction band to Pt and hindered undesired charge recombination [2].

In Example III in situ EPR spectroscopy was used to identify active sites for photocatalytic hydrogen generation in modified $Y_2Ti_2O_7$ and $CsTaWO_6$ catalysts of pyrochlore structure, in which the metal cations are located in two different positions A and B. It was found that the B-sites exclusively occupied by titanium ($Y_2Ti_2O_7$) and tantalum/tungsten ($CsTaWO_6$) act as electron traps on the surface, making them active for photocatalytic water reduction [3].

References

[1] J. Xiao et al., ACS Catal. 9, 8852 (2019); Acc. Chem. Res., under review.
[2] R. Sivasankaran et al., Catalysts **8**, 52 (2018); Catalysts, **9**, 695 (2019).
[3] D. Hoillmann et al., Top. Catal. **58**, 769 (2015).

Charge generation via hole transfer in fullerene-based bulk heterojunction solar cells – A first-principles rate-theory approach complementing recent multispectral 2DES experiments.

A. Schubert[1,2,3], **Y. Song**[4], **S. Bhandari**[3], **J. P. Ogilvie**[4], **E. Geva**[2], **B. D. Dunietz**[3]

[1]*Institute of Physical Chemistry, Friedrich Schiller University Jena, Germany*
[2] *Department of Chemistry, University of Michigan, USA*
[3] *Department of Chemistry and Biochemistry, Kent State University, USA*
[4] *Department of Physics, University of Michigan, USA*

For efficient organic photovoltaics (OPV) a broadband photoabsorption that exploits all charge generating pathways would be highly desirable. While electron transfer from organic donors to acceptors is well investigated in numerous studies, much less is known about hole transfer pathways. Here we theoretically investigate an archetypal system comprising tetraphenyldibenzoperiflanthene(DBP):C70 blends by means of time-dependent density functional theory (TDDFT) employing a recently developed polarization-consistent framework based on screened range-separated hybrid functionals and the polarizable continuum model (SRSH-PCM). Based on such first principles calculations, the fully quantum-mechanical Fermi's golden rule (FGR) rate theory is applied to simulate the complex multi-state transition kinetics leading to photo-induced charge generation at the donor-acceptor interface.

Our simulations support the interpretation of recent multispectral (Vis+NIR) two-dimensional electronic spectroscopy (M-2DES) measurements revealing two charge transfer pathways originating in donor and acceptor excitons. We find that both, electron and hole transfer, occur with comparable rates and efficiencies. Our results highlight the importance of hole transfer pathways for optimizing the efficiency of small-molecule heterojunction OPV devices.

Accessing chiral dynamics via broadband time-resolved circular dichroism spectroscopy

Lea Ress[1], **Heiko Hildenbrand**[1], **Hope Bretscher**[2], **Akshay Rao**[2] **and Tobias Brixner**[1]

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Time-resolved circular dichroism (TRCD) spectroscopy is a useful technique to understand configurational and conformational changes in chiral systems. It enables to investigate the ultrafast dynamics of photoinduced chirality changes on a sub-picosecond timescale. We use a pump–probe approach by exciting the sample with a linearly or circularly polarized pulse and probe the difference in absorption of left- and right-circularly polarized pulses on a shot-to-shot basis. For this, we developed a setup that is capable of mirroring the polarization state of an ultrashort broadband laser pulse [1]. This is achieved by splitting the incident beam into two separate beams of which one is mirrored by reflecting off a mirror in normal incidence. Thereafter, both beams are recombined in time and space so that two collinearly propagating ultrashort laser pulses with mutually mirrored polarization, i.e., laser-pulse enantiomers, are leaving the setup. Since the two beams travel separately through the setup, shot-to-shot chopping and detection schemes can be applied and enables us to simultaneously acquire data of transient CD and absorption changes.

Here we demonstrate TRCD spectroscopy of monolayer MoS_2 as a proof of principle experiment, validating the setup with respect to literature results [2]. In addition to spectroscopy of surfaces, we also investigate the change in chirality of a perylene bisimide folda-dimer in solution [3]. Furthermore, we analyze the arrangement of chiral surfactants around the achiral dye Congo red and the ultrafast change in chirality after excitation.

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Potential of the pulsed field gradient NMR for direct probing of the ionic dynamics in materials for supercapacitors

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The ionic diffusion in energy storage devices, such as, e.g., supercapacitors, enables their charging and discharging ability. In the milestone contribution of Chmiola et al. [1], it has been demonstrated that higher values of the specific energy are achieved in carbons with pore sizes being comparable to those of adsorbed ions. However, under such constraints, one may expect kinetic problems caused by confinement-induced obstruction for molecular diffusion.

Only very recently, the direct experimental assessment of the ion dynamics within the pores of carbon materials became possible by means of the quasielastic neutron scattering [2] and the pulsed field gradient (PFG) NMR [3]. Inspired by these novel methodological achievements, we succeeded to directly measure the ionic dynamics of organic electrolytes and ionic liquids confined to model carbons using the PFG NMR with ultra-high gradients [4]. Quite unexpectedly, we observed that the presence of a network of mesopores, in addition to smaller micropores—the concept widely used in heterogeneous catalysis to promote diffusion of sorbates—does not necessarily enhance ionic transport in carbon materials.

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Electronic Systems under Elementary Spatio-Temporal Confinement

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Studies of the quantum dynamics of electrons which are confined to elementary dimensions of space and time will be presented. Single electrons excited in individual semiconductor quantum dots are studied in the first part, aiming at single-photon amplification for the ultimate control of the quantum statistics in ultrashort light pulses [1]. In these systems, the ultrafast dynamics of electrons and holes is dominated by fundamental aspects of quantum physics such as Coulomb correlations and the Pauli principle [2,3]. Based on a pump-probe system optimized for single-electron sensitivity at low temperatures and high magnetic fields [4] we were recently able to study specimens with extremely asymmetric relaxation channels in valence and conduction bands, where femtosecond quantum kinetics of hole-phonon coupling and sub-nanosecond intraband coherence of electrons occur. The second part introduces the concept of transient Wannier-Stark localization. Here we are able to induce a two-dimensional character in the electronic system of a bulk semiconductor by lifting the chemical bonds in the direction of subcycle electric fields of intramolecular strength lasting only a few femtoseconds [5]. Finally, we will control the transport of single electrons with phase-locked single-cycle pulses in the near infrared applied to plasmonic nanoantennas [6]. The attosecond dynamics of electronic currents in a few-nanometer gap between metallic contacts is studied both in experiment and theory [7,8]. An outlook will be given, presenting the status of our efforts to investigate quantum transport phenomena at truly atomic spatio-temporal scales.

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Combining different spectroscopies to quantify the flow of electrons in quantum dot films

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Quantifying excited state dynamics is the key to designing and improving materials for optoelectronic devices. Specifically, understanding the competing processes (i.e. radiative vs. non-radiative recombination, multiple exciton generation, charge transfer and extraction) for excited states in quantum dot (QD) films and solar cells is critical for finding and fixing defects in them. Here we use a combination of spectroscopic techniques: transient absorption, time-resolved microwave conductivity, spectroelectrochemistry, time-resolved photoluminescence and photoluminescence quantum yield (PLQY) to understand the transport and fate of excited charge carriers. The optoelectronic properties of the QDs depend largely on the surface environment of the nanocrystal. The molecules (i.e. ligands) present on the surface from the synthesis of the QDs often hinder certain desirable processes like charge transfer and induce undesirable effects like charge carrier recombination. In order to make the highest performance materials in terms of solar cell efficiency or PLQY, the ligands are exchanged for others. We present our findings on how certain properties like charge carrier transport, PLQY, and carrier multiplication efficiency are affected by the nature of the surface ligands. We show spectroscopic and device performance data for three general types of QDs: PbS(e), CdTe, and In(Zn)P and provide a general strategy for improving performance by employing a combination of theoretical and experimental techniques to find and fix the limiting processes.

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Time-resolved photocurrent measurements

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In modern information technology, data is processed as electrical signals by a computer and transmitted as pulsed photonic signals in optical fibres. In this process, optical switches are one of the major limiting factors as they perform the crucial task to convert light pulses into electrical signals. To assess the prospects of a new active material for optical switching, its impulse response to short light pulses in the nanosecond to picoseconds regime needs to be characterized. In addition, complementary information on the switching properties can be gained from square pulse illuminations. We have recently developed a setup that can perform both kinds of measurements with a time resolution of approx. 1.7 ns. This setup affords the simultaneous impulse and square pulse characterization of new materials and allows more detailed insights into the expected performance of optical switches than previous investigations operating with just one of the two techniques.

To illustrate this, we will present results on a recently investigated optical switch consisting of inorganic nanoparticles and organic semiconductors. The active material is composed of CdSe nanocrystals, sensitized with Zinc β-tetraaminophthalocyanine, for operation both under visible light and in the first telecom window. Our time-resolved photocurrent measurements reveal fast step response rise times of 74 ± 11 ns under near-infrared optical gating with 780 nm.[1] This is significantly faster than observed for other materials with strong absorption in the near-infrared, such as HgTe-CdS nanoplatelets (10 µs) or PbSe NC nanojunctions (300 ns).[2,3]

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Broadband Two-dimensional Electronic Spectroscopy with a Birefringent Interferometer

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A wealth of novel information on molecular structure and dynamics can be obtained by extrapolating 2D techniques, commonly used in NMR, to the optical domain [1]. 2D spectroscopy is the "ultimate" ultrafast optical experiment, since it provides the maximum amount of information that can be extracted from a system within third-order nonlinear spectroscopy. The first applications were with IR pulses, resonant with vibrational transitions. Recently, 2D optical techniques have been extended to the visible and UV ranges, targeting electronic transitions. 2D electronic spectroscopy (2DES) allows fundamentally new insights into the structure and dynamics of multi-chromophore systems, measuring how the electronic states of molecules within a complex interact with one another and transfer electronic excitations [2]. By spreading the information content of the nonlinear signal on two frequency axes, 2DES allows: (i) to measure the homogeneous linewidths of optical transitions, enabling to single out the individual levels in strongly congested spectra; (ii) to separate contributions to the nonlinear signal that are spectrally overlapped in the 1D experiments; (iii) to overcome the Fourier limit and to obtain simultaneously high temporal and spectral resolution; (iv) to directly observe and quantify couplings between different excited states, which appear as cross peaks in the 2D spectra; (v) to follow in real time the pathways by which the coupled electronic/nuclear dynamics within a complex multi-chromophoric systems evolve after photoexcitation, and to track energy/charge transfer processes.

This presentation will review the experimental techniques currently used to perform 2DES in the visible range and we will present our approach to 2DES, based on a passive birefringent interferometer for the generation of phase-locked pump pulses [3]. We will present a few exemplary results on multi-chromophoric systems and nanostructures [4-6] and finally discuss the prospects of extending 2D techniques to the UV range, of interest for biomolecules such as DNA and proteins.

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Simulation of optical spectra in the time-domain

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In this contribution I will give an overview over recent efforts for the quantum chemical simulation of spectroscopic experiments from an atto second to pico second time scale covering electron and nuclear dynamics.

Complementary to frequency domain approaches in recent years simulations in the time domain gained a lot of interest for the simulation of molecular systems.

These time domain approaches recover the energy domain information via auto correlation functions and Fourier transforms.

Specifically, recent developments of the simulation of vibrational spectra using *ab initio* molecular dynamics [1] in the condensed phase will be discussed [2]-[4].

Moreover real time time dependent density functional theory (RT-TDDFT) techniques [5] will be presented for the calculation of absorption, electric circular dichroism [6], (resonance) Raman [7] and Raman optical activity [8] spectra, with special attention to the problem of gauge origin, which appears in practical TDDFT calculations.

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Semiconductor, insulator, or molecule – do we understand excitation and transport in "graphitic carbon nitride"?

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During the last decade, polymeric "graphitic" carbon nitrides (CN) have gained a lot of interest, especially as metal-free photocatalysts for solar-driven water splitting and other catalytic reactions. Despite many efforts in synthesis and material analysis, their catalytic performance remains comparably low. It is therefore important to systematically understand the photophysics in CNs.

Composed of either triazine or heptazine motifs, CN polymers form structures ranging from highly crystalline to almost amorphous. Their behaviour is hence dominated both by the physics of the structural motifs (i.e., the monomers), as well as by the emergent properties of the meso- and macroscopic bulk material.

In this presentation, we show how to gain insight into the generation, transport, and ultimate fate of photoexcited species using complementary time-resolved optical spectroscopies, namely photoluminescence and transient absorption. By analysing data obtained over more than 12 orders of magnitude in time, these techniques have revealed fascinating physics: molecular-exciton-like absorption and emission,[1] diffusive transport of polaronic (?) carriers,[2,3] as well as dimensionally confined transport scenarios.[2,4] We will contribute to the ongoing discussion, whether these phenomena are best described using molecular, insulator, or semiconductor pictures.

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Electron Transfer Reorganization Energies in the Electrode-Electrolyte Double Layer

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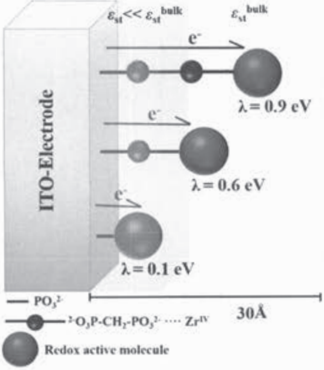

Elucidation of electric double layer (EDL) structure at solid-liquid interfaces continues to be of intense theoretical and experimental interest due to its importance in electrochemistry, catalysis, and biology. The classical work of Grahame established that water molecules within the EDL differed significantly from bulk water.[1] In particular, the first water layer at a Hg electrode was shown to have an effective dielectric constant ε_{st} ~8, while that of bulk water is ε_{st}^{bulk} ~80. Dielectric continuum theory predicts that the solvent reorganization energy, λ_o, approaches zero within the Helmholtz planes of polarized electrodes.[2] To our knowledge, this important prediction has not been validated experimentally. Herein, we report heterogeneous electron transfer (ET) from a conductive oxide (In_2O_3:Sn, ITO) to redox-active molecular acceptors within the EDL as a function of driving force $-\Delta G^o$, from which the total reorganization energy, λ, was extracted.[3] Excited-state injection into ITO generated a molecular acceptor on sub-nanosecond time scales, and the ET kinetic rate constant, k_{et}, was quantified spectroscopically. In agreement with dielectric continuum theory, Marcus-Gerischer analysis of the kinetics revealed that λ within the diffuse layer increased with distance to values expected for fluid solution, λ = 0.9 eV. The ET kinetics were remarkably insensitive to $-\Delta G^o$ when the acceptor was within the outer-Helmholtz plane, consistent with λ = 0.1 eV. The data reveal small intrinsic barriers for electron transfer proximate to conductive interfaces, exploitable behavior in solar energy conversion and other applications that utilize transparent conductive oxides to accept or deliver electrons.

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Coherent spectroscopy of near-infrared materials

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Modern active media of semiconductor opto-electronic devices are based on tailored nanostructures of different dimensionality. Future device concepts based on such nano-materials require a deep understanding of the interaction of photonic and electronic states, especially, if complex potential landscapes evolve. Simplified level schemes often do not capture the essential coupling and scattering pathways. Advanced heterodyne pump-probe techniques were developed and merged into broad-band 2D-coherent spectroscopy to study quantum state coupling within a wide energy range. We apply these NLO-techniques to NIR-materials like InAs QDs, PbS/CdS NCs and transition metal dichalcogenides (TMDs). The use of spectrally broad probe fields allows us to investigate coherently coupled exciton states with large energy separation up to ~200meV.

Examplary, we report about so-called "crossed excitons", i.e. 0D-excited states resonant to the 2D continuum which could be detected by two-dimensional four-wave mixing spectroscopy [1-3]. A second example are colloidal NIR-emitting nanocrystals (PbS/CdS core-shell QDs) deposited on a silicon nitride waveguide and investigated for their charge carrier dynamics [4]. Third, a study of submonolayer (SML) QDs formed by vertically correlated in-rich islands in a GaAs matrix was performed. SMLs present a gain medium with exceptionally large amplitude-phase coupling. In addition to a large α-parameter, SML QDs display excellent broadband features and a large optical gain in the important 1060 nm spectral window and they are very promising for the generation of chaotic emission patterns upon optical feedback [5]. Finally, we investigate valley dynamics associated with excitons and trions in monolayer TMDs using polarization resolved spectroscopy. Exceptionally robust valley polarization associated with resonantly created intravalley trions are discovered and may be explored for future valleytronic applications [6].

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Two-beam Ultrabroadband Coherent Anti-Stokes Raman Scattering Spectroscopy for Temperature and Concentration Measurements Using a Dual-output OPCPA

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Gas thermometry and concentration measurements under high temperature and pressure is of great importance for applications in gasification or combustion [1]. Femtosecond/picosecond coherent anti-Stokes Raman scattering (fs/ps CARS) has been proved to be an ideal approach for non-invasive temperature measurements [2]. By applying a proper probe delay, one can efficiently suppress the unwanted non-resonant signal, moreover, the picosecond probe beam balances a sufficient CARS spectral resolution and a detection time window which the high-pressure collisions may be neglected. In this case, we implement gas temperature and concentration measurements based on a two-beam vibrational ultrabroadband fs/ps CARS setup. Originated from a dual-output optical parametric chirped-pulse amplification (OPCPA) system, a ~7 fs ultrabroadband beam (~(650–1100) nm) is used as pump/Stokes pulses to achieve ultrabroadband excitation for multiple molecules, and an additional ~2 ps beam is used as probe pulses.

Based on the current setup, we show the capability of simultaneous detection of the most relevant combustion species. The temperature measurements are implemented and compared simultaneously from N_2, CO_2 and H_2 at 1.7 bar. The best performance is given by CO_2 CARS spectrum, resulting in an accuracy and a precision within 4.2% and 0.7% for temperatures from 295 K to 1000 K. From 10 bar to 20 bar, the temperatures are measured up to 500 K with an accuracy within 3.6%. The concentration measurements are also implemented in multiple gas mixtures. At ~1.5 bar, we demonstrate a detection limit of 2% CO (determined to be $(2.2 \pm 1.0)\%$) at 1073 K in CO/CO_2 gas mixtures and a detection limit of 0.5% CO (determined to be $(0.5 \pm 0.3)\%$) at 295 K in $CO/CO_2/N_2$ gas mixtures.

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Strong laser field induced Coulomb explosion of clusters and droplets: Exploring the dynamics from atto- to microseconds

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Excitation of clusters by intense laser pulses triggers the Coulomb expansion of the developing nanoplasma. Controlling the laser field and mapping the electron and ion signals allows to characterize but also steer the dynamics on vastly different timescales. Two-color pulses can be applied to control the electron emission with attosecond resolution [1]. Femtosecond pump-probe excitation allows for the production of highly charged atomic ions in the plasma expansion via resonant plasmon excitations [2]. In the talk, I will focus on the longer times, where correlated electronic decay leads to Auger emssion [3]. The characteristc patterns give information about the temporal development of the plasma potential. Finally, on the timescale of microseconds, charge state and energy resolved ion spectroscopy reveals signals from highly charged ions in highlying Rydberg states [4]. Hence, by monitoring the multiple features observed in the emission spectra, the full temporal evolution of a transient warm dense matter system can be traced.

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Macromolecular diffusion dynamics on the nanometre scale studied with MIET

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Fluorescence correlation spectroscopy (FCS) is a powerful tool to probe translational diffusion times and fast dynamic processes of fluorescently-tagged macromolecules freely diffusing in solution. Classical FCS offers an accessible time range limited by the diffusion time of the probe, which can be extended by immobilising the molecules on a surface and slowly scanning with a focused laser beam.[1] We combine FCS with metal induced energy transfer (MIET), which has already been utilised to localise fluorescent emitters axially with nanometre accuracy.[2] MIET relies on quenching of the excited-state fluorescence lifetime and intensity of a fluorophore by a near-field coupling mediated energy transfer to a thin conducting metal film. This quenching behaviour shows a strong distance dependence over a range of 0 to 150 nm from the metal surface and results in a distance-dependent modulation of fluorescence lifetime and brightness. By analysing the intensity fluctuations with scanningFCS, the vertical diffusion timescales of tethered macromolecules and polymeric chains can be quantified. For a synthetic polymer brush, we found vertical diffusion on the microsecond which depends on the swelling of the brush. Additionally, we demonstrate how this technique can be used to measure dynamics over a broad range of timescales. For this purpose, we use tethered DNA-hairpins for which dynamic processes from the tens of nanoseconds to the millisecond scale can be resolved, including the vertical diffusion the sub-microsecond scale and the hairpin formation at a few milliseconds.

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Attosecond Science: Opportunities and Challenges for Measurements at the Limit

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With progress towards ever shorter laser pulses we have developed many different pump-probe techniques to access fast dynamics with the time resolution approximately given by the duration of the laser pulse. With the discovery and understanding of high-harmonic generation (HHG) we were able move into the attosecond domain. The orbital period of an electron in ground-state hydrogen in Bohr's model amounts to 150 as. The attosecond is thus the typical time scale for electronic motion on an atomic scale. The much higher inertia of atomic nuclei prevents them from exhibiting similarly fast dynamics under normal conditions[1].

The generation of attosecond pulses and their application to time-resolved studies have remained challenging in comparison to the femtosecond domain. Nanojoule pulse energies 100-MHz pulse repetition rate corresponds to 100-mW average power, whereas at 1-kHz to 1 µW, reducing signal-to-noise by 5 orders of magnitude. Thus efforts for higher pulse repetition rates, higher pulse energy and/or higher photon energies are ongoing in many labs but also at new user facilities such as ELI, SwissFEL and others, providing new opportunities to enter the attosecond measurement frontier. We want to extend attosecond science to more complex molecular or solid-state systems and to investigate some of the most fundamental aspects in physics and chemistry finding answers to long-standing ultrafast processes that were considered "instantaneous" before.

After a general introduction this keynote talk will discuss some results in my group using mixed infrared/XUV pump-probe techniques to study ionization dynamics (atoms[2], molecules[3], solid surfaces[4]) and petahertz spectroscopy in diamond[5], GaAs[6] and Ti[7]. We have invented the attoclock[8] as an alternative technique to address very fundamental questions in quantum mechanics such as tunneling time[9], time delays between electrons in double ionization[10], and momentum transfer to photoelectron in multi-photon ionization[11].

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Deciphering the structure, dynamics, and chirality of complex molecules

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The precise knowledge of the structures of molecules and their ability to form dedicated non-covalent intermolecular interactions is of fundamental use for understanding their function. High-resolution rotational spectroscopy provides an outstanding tool to determine accurate molecular structures in the gas phase and thus free of solvent and crystal effects. These conditions allow for a direct comparison and benchmarking with quantum-chemical experiments.

Of particular interest for us are the roles of conformational flexibility, non-covalent interactions, and chirality in molecular processes. We use broadband rotational spectroscopy (complemented by quantum-chemical calculations and other spectroscopy techniques) to evaluate how molecules bind to each other and to establish a hierarchy of intermolecular interactions. These studies are also relevant with respect to the first steps of aggregation, such as in soot and grain formation, and can thus provide important insight into the transition from the isolated molecule to the bulk.

In a related branch of research, we focus on characterizing, controlling, and finally manipulating chirality. Using the microwave three-wave mixing approach, which is non-linear and resonant, we can differentiate enantiomeric pairs of chiral molecules using tailored microwave pulses. The technique is uniquely mixture-compatible and allows for enantiomer separation, as will be discussed.

Triplet fusion photon upconversion: at the intersection of photonics and photochemistry

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Triplet fusion is a photochemical process in which two quanta of electronic energy become combined within a single chromophore. When implemented in a suitable material system, triplet fusion enables photon energy upconversion – the emission of photoluminescence with a considerable anti-Stokes shift (of the order 1eV) with respect to the photoexcitation source [1]. The process begins with the optical excitation of spin-1 (triplet) excitons, via a triplet sensitizer material; then the transfer into and diffusion throughout a so-called annihilator material. Triplet-triplet encounters within the annihilator lead to triplet fusion; the resulting high-energy state can then relax via photoluminescence, or energy transfer to a reaction center. Photon upconversion has technological applications in photovoltaics, artificial photosynthesis, imaging, and phototherapies [2]. The concerted interaction between photochemistry, photonics and material interfaces, which underpins the photon upconversion process, makes this a lively research topic with contributions possible from many disciplines. With this broad scope in mind, we present an overview of the current status of triplet fusion upconversion materials and applications.

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Time-Resolved Serial Crystallography: Watching Proteins in Action from Femtoseconds to Seconds

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To fully capture the dynamics and structural changes during biochemical reactions over several orders of magnitude in time, is a major experimental challenge and became recently accessible by time-resolved serial femtosecond crystallography (TR-SFX), driven by the availability of XFEL sources.

The sample delivery tools originally developed for those studies at XFELs on the ultrafast time scale [1, 2] start to inspire similar experiments at synchrotrons [2, 3], thereby enabling time-resolved serial synchrotron crystallography (TR-SSX), which allows the study of protein dynamics on time-scales >us at ambient conditions.

We have recently demonstrated the *hit-and return* (HARE) approach [4], which uses fixed targets for sample delivery of up to 25.000 protein crystals on an individual crystallography chip and allows the efficient data collection for several time points during a single synchrotron beamtime. Using the HARE approach, we were able to follow the full reaction cycle of an enzyme, fluoroacetate dehalogenase, and captured 18 time points from 30 milliseconds to 30 seconds during the non-reversible turnover, resolving the full catalytic reaction and observing a previously unknown allosteric mechanism based on interfacial water connecting the subunits [5].

Crucial for this experiment was the efficient reaction using a photocaged substrate, thereby allowing to study light-insensitive, irreversible processes [4,6].

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Excitons are stable in ultrathin CdSe nanoplatelets: Even at high density!

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We studied excitons and charge carriers in CdSe nanoplatelets with thickness of a few atomic layers and lateral sizes of tens of nanometers. Excitons and charge carriers were generated by photoexcitation with ultrashort laser pulses and detected by time-resolved optical absorption and terahertz conductivity measurements.

Photoexcitation leads predominantly to formation of excitons with 2D translational centre-of-mass motion that can be described using the simple particle in a box model. Theoretical analysis of time-resolved optical absorption and terahertz photoconductivity data provides information about the quantum yield and polarizability of excitons, as well as the mobility of charge carriers.

Interestingly, excitons in CdSe nanosheets are stable even at high densities where they start to exhibit spatial overlap. A crossover to an electron-hole plasma of uncorrelated free electrons and holes is not observed. This counter intuitive result can be understood theoretically from the fact that the Coulomb screening length, and thus the exciton binding energy, remain non-zero even at high density. This is a particular result for 2D materials, which does not hold for 3D semiconductors.

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Abstracts of Posters

(in alphabetical order)

Time dependent IR induced action spectroscopy of sodium doped water clusters

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Water clusters are model systems bridging the gap from gas phase to the bulk. They reveal information about size dependent properties of hydrogen bonding, e.g. transition from amorphous to crystalline bonding motifs [1].

Mass spectrometry is commonly used for size selection, but can comprise some difficulties: On the one hand direct photoionization causes fragmentation, on the other hand electrospray ionization produces clusters, whose bonding network may be disturbed by (highly charged) metal ions.

In an approach, developed by Buck and used in our group, neutral water clusters are produced via supersonic expansion and doped with a single sodium atom afterwards. It was shown that the ionization energy depends on extent of microsolvation and that this microsolvation is a function of cluster temperature [2].

Therefore heating up clusters by means of a monochromatic IR laser pulse enhances the ion yield of clusters and therefore IR-action-spectroscopy of neutral water clusters is enabled.

In this study, the delay between IR heating pulse and soft UV-ionization pulse was varied. Cluster evaporation is observed for long delays, which is more pronounced at the absorption maximum of amorphous species. Therefore, not only size selection, but also a method for isomer selection in terms of amorphous and crystalline clusters may be enabled.

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Transient absorption spectroelectrochemistry on dye-sensitized photocathodes

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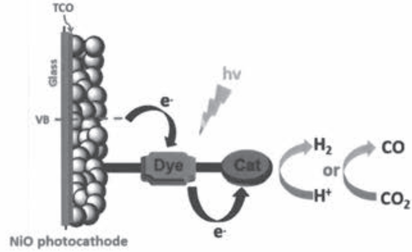
Long charge-separated state lifetimes are essential for efficient dye-sensitized photocathodes used in dye-sensitized photoelectrochemical cells (DSPEC), used for water splitting or CO_2 reduction.[1] Transient absorption spectroscopy can be used to investigate light-induced processes such as charge injection and charge transfer to the catalyst as well as charge recombination and thus the lifetime of the catalytically active state.[2,3] By further applying a potential bias in a transient absorption spectroelectrochemistry (TA-SEC) measurement, systems can be studied under conditions close to the operando conditions in photoelectrochemical tests.[4,5]

TA-SEC measurements on NiO films sensitized with Ruthenium-based and organic sensitizers covalently bound to a cobalt catalyst active for the reduction of protons to molecular hydrogen were performed using a newly built spectroelectrochemical cell. Charge separation and electron transfer as well as as charge-separated state lifetimes could be determined and show heavy dependence on the applied potential. Charge-separated state lifetimes at applied reductive potential increased by up to four orders of magnitude into the microsecond scale, finally allowing a correlation of light-induced process kinetics determined by spectroscopy with the observed catalytic performance of the systems under photoelectrochemical conditions.



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It takes three to tango-Investigating the excited state properties of TLD-1433 family with increasing thiophene chain length

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We report the excited state properties of TLD-1433(Ru-ip-3T) and its family (0-4) with increasing thiophene chain length in water. TLD-1433 is the first Ru(II) complex to enter human clinical trial as a PDT drug for bladder cancer treatment[1]. CV measurements highlight increasing HOMO and unaltered LUMO energies with increasing chain length. This is line with the red shifted LC band in the UV-visible absorption spectra with increased percentage of LC contribution for higher members. Emission quantum yield measurements show systematic decrease with increasing chain length with all emissions centered at 640 nm typical for ^{3}MLCT emission for Ru(II) polypyridyl complexes. Absence of LC band in the excitation spectra of Ru-ip-3T/4T closely resemble to those of Ru-ip/1T which do not populated LC states. This further correlates with similarity of emission lifetimes for all with the exception of Ru-ip-2T which displays long lived mono and bi-exponential decays under aerated and degassed conditions respectively. These results are rationalized by coupled ^{3}MLCT-^{3}LC states for Ru-ip-2T due to nearby energies. However, addition of the third thiophene ring stabilizes the ^{3}LC further and decouples these states resulting in two independent channels for deactivation. Generation of singlet oxygen increases with increasing chain length in line with increased photo cytotoxicity for higher analogues.

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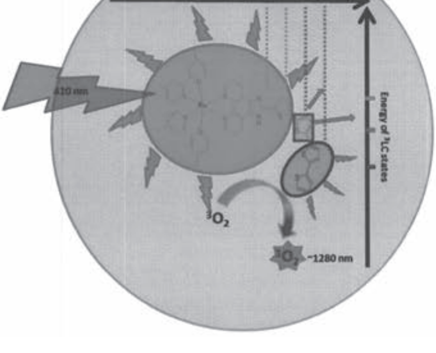

Tailored phenanthroline-based ligands for heteroleptic copper(I) photosensitizers

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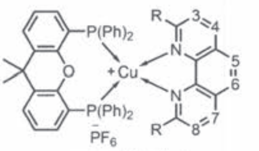
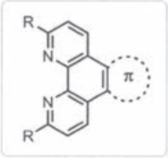
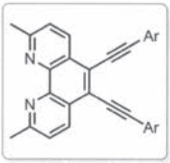
Heteroleptic diimine–diphosphine Cu(I) complexes of the type $[(P^\wedge P)Cu(N^\wedge N)]^+$ (see general structure below) represent a viable alternative to commonly used noble-metal containing photosensitizers like $[Ru(bpy)_3]^{2+}$. A major drawback of such heteroleptic Cu(I) systems, however, is their limited ability to efficiently absorb visible (sun)light.[1] To tackle this issue, several studies already dealt with the introduction of fused aromatic rings in 5,6-position at the phenanthroline moiety (*cf.* below).[2,3]
As a result, the absorption intensities were increased, but the absorption maxima were only slightly shifted to the visible. In addition, the fused aromatic rings caused a decrease in the emission lifetimes and a significant shift in the redox potentials.[2,3]



general structure



previous studies
fused aromatic rings



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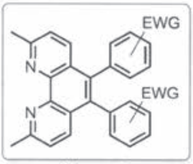
alkynyl-based



this work
phenyl-based

Recently, we have chosen an alternative way by introducing different alkynyl-based (*e.g.* ethynyl-4-fluorobenzene) and phenyl-based (*e.g.* 4-fluorobenzene) substituents in 5,6-position *via* Suzuki-Miyaura and Sonogashira cross coupling reactions. Consequently, a systematic series of 11 novel heteroleptic Cu(I) complexes were prepared and investigated by various photo- and electrochemical methods. Interestingly, one heteroleptic complex showed a tenfold increase in emission lifetime compared to the unsubstituted reference, demonstrating the tunability of these photosensitizers. The reasons for this behaviour are still under investigation.

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Anisotropic Nanocrystal Growth from Local Monomer Hotspots

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Anisotropic semiconductor nano-heterostructures are available e.g. in the form of seeded[1] or tipped rods.[2] While literature is able to provide several synthetic routes towards such structures, mechanistic studies on the emergence of anisotropy scarce. The leading hypothesis assumes fast growth at high monomer concentration under reaction control and the influence of selectively passivating ligands.[3] However, recently the role of reaction intermediates such as magic size clusters (MSCs) and coordination polymers (CPs) has come into focus.[4]

We show that polymeric reaction intermediates act as monomer reservoirs that result in a highly localized rather than homogeneous concentration of monomer in the reaction solution. They decompose preferentially at the reactive facets of a seed particle, which leads to 1D growth at the respective crystal facet, and consequently an increase in anisotropy. The change in concentration of the transient species is the key to understanding the regioselective reaction mechanism of the formation of anisotropic particles.

A good understanding of reaction paths that lead to anisotropy is mandatory to achieve an additional level of control over particle morphology. Furthermore, it opens up a new range of precursors that can be manipulated by chemical means and thus allows for the synthesis of more complex structures, e.g. branched or locally doped heterostructures.

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A ps time-resolved photoelectron imaging study on the photophysics of tolane

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Photoelectron spectra recorded via resonance-enhanced multiphoton ionization (REMPI-PES) contain information on the structure of excited neutral states, since the kinetic energy distribution of the photoelectrons is highly sensitive to the electronic character of the neutral molecule. Time-dependent changes in the spectra thus also yield information on relaxation dynamics after photoexcitation. The combination of small bandwidth ps laser pulses and supersonic jet expansion allows us to excite zero order vibronic states of cold molecules and to elucidate their dynamics.

The subject of our present study is tolane (diphenylacetylene, $C_{14}H_{10}$), a fundamental building block for conjugated polymers or dendrimers. The interest on the photophysical properties of tolane is based on its unusual fluorescence, which breaks down after exciting vibronic modes higher than 700 cm^{-1} above the origin of the first bright excited state ($^1B_{1u}$).[1, 2] The low-energy part of our S_1 ($^1B_{1u}$) $\leftarrow$ S_0 REMPI spectrum is very similar to earlier recorded LIF spectra,[1, 2] however additional bands were observed at higher energies above the fluorescence cut-off. For a number of bands the dynamics were investigated via pump-probe photoionisation and photoelectron spectroscopy. Around the B_{1u} origin the lifetimes are in the ns range, but they drop to some 10 ps at higher excitation energies. For the short-lived bands at higher energies a sequential two-step relaxation to a long-lived electronic state was observed that proceeds via an intermediately populated state with a lifetime of 100-200 ps. By comparison with previous quantum chemical calculations we assign this state as the biradicalic *trans-bent* ^1A_u state that is ionised in a two-photon process via an intermediate 3p Rydberg state.

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Direct observation of negative Goos-Hänchen shift and plasmon coupling in self-assembled semiconducting polymer microspheres on a plasmonic substrate

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Self-assembled semiconducting microspheres made of π-conjugated polymer support whispering-gallery modes (WGMs) in the visible range [1]. These organic semiconducting microspheres represent a unique kind of laser cavities, which offer the largest possible gain concentration, high quality-factor, high refractive index, and the possibility of electrical pumping. To electrically pump such organic semiconducting microspheres, the physical contact to the conductive substrate can, however, alter the optical properties of the microcavities. In this work, we perform excitation position-dependent spectroscopic analysis on the emission of single semiconducting polymer microspheres on various conducting substrates, including ITO, gold, and graphene. We show, for the first time, direct observation of negative Goos-Hänchen shift and plasmon coupling in a single self-assembled semiconducting polymer microsphere on atomically flat gold surface. The success of this spectroscopic study is based on the fact that the excited polymer molecules are spatially confined at the surface of the spheres due to the high concentration and high absorption cross section at the excitation wavelength. Therefore, we can selectively excite different WGMs by controlling the position of the tightly focused laser spot. This grants the opportunity to reveal the substrate effect on the emission spectrum. Our work gains insight into the influence of the conductive substrate on the WGMs for the realization of electrically pumped WGM lasers.

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Lead Chalcogenide Nanoplatelets and their Optoelectronic Properties

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Anisotropic semiconductor nanoparticles show interesting optoelectronic properties differing from spherical properties. Especially two-dimensional nanosheets and nanoplatelets are an exceptional class of nanoparticles with intriguing characteristics such as a small Stokes-shift and a small FWHM. Due to their one-dimensional quantization the electronic properties differ notably from the bulk material. For instance, the suppressed Auger recombination enables the application in lasing[1], whereas the decreased shielding results in increased exciton binding energies[2]. Characterising these properties demand sophisticated spectroscopic methods with a good time resolution e.g. in optical pump-probe experiments.

Lead chalcogenides are a potent class of materials for the development of optoelectronic nanoparticles. Their small bandgaps lead to optical properties in the NIR range unachievable by e.g. cadmium chalcogenides. This could prove beneficial e. g. in photovoltaics or sensors.[3] We show the optoelectronic properties of different lead chalcogenide nanoplatelets and provide ways to further tailor the nanoplatelet synthesis to achieve optimal properties.

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Synthesis and optoelectronic properties of two-dimensional colloidal nanomaterials

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I will present a poster with an overview about our group's research efforts as a basis for discussions [1].

Two-dimensional colloidal nanomaterials have gained more and more attention as attractive optoelectronic materials in the recent years. They combine good lateral conductivity with solution-processability and geometry-tunable electronic properties. The formation of ordered and densely packed surface layers of amphiphilic ligand molecules on certain crystal facets can drive the normally isotropic into a two-dimensional crystal growth, resulting in semiconducting nanosheets. Due to the strongly reduced height, such metastable materials are in electronic confinement, which allows tuning their effective bandgap. Other features are reduced charge screening, efficient doping, and solution processablility. I will present the syntheses of the materials, followed by analyses of their optical properties and the electrical transport characterization through these materials as field-effect and spin transistors. In particular, I will introduce nanosheets based on lead sulfide, tin sulfide and lead halide perovskites. The materials show surprising effects and demonstrate the versatility and usefulness of this synthesis approach.

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Angular resolved photoemission of metal atoms embedded in helium nanodroplets in the MPI regime

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Angular resolved photoelectron emission spectra of single metal atoms embedded in helium nanodroplets are measured, analyzed and compared to free atoms. A femtosecond laser system provides 110 fs, linear polarised laser pulses, which are used to ionize the atomic targets in the multiphoton regime ($I \approx 10^{13...14}$ W/cm²) without ionizing the helium nanodroplet itself. Furthermore a time delay controlled two color setup with overlapping 2ω/ω (400 nm/800 nm) fields is used to probe the attosecond dynamics. For this we apply the highly sensitive Phase-of-the-Phase (*PoP*) method [1], which has been previously used to extract information about photoelectron trajectories. Compared to the anisotropic above-threshold-ionization (ATI) signals from free atoms a near isotropic emission is obtained for the embedded species. Furthermore, an enhancement of ATI signals and additional ATI orders can be observed. In the same vein we see a reduction of relative phase contrast. The impact of elastic scattering of the electrons with the surrounding helium environment will be discussed.

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Monitoring the growth of CdSe/CdS giant-shelled nanocrystals by spectroscopic measurements

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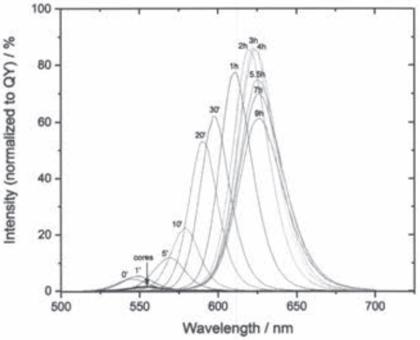
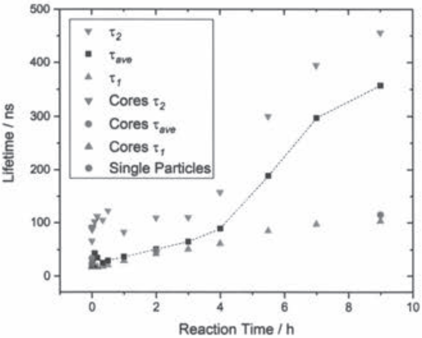
Based on the synthesis from Bawendi et al. [1] we developed a synthesis for CdSe/CdS giant-shelled nanocrystals with adjustable diameter from 8-20 nm. By analytical in situ characterization and systematic parameter variation, we got the key knowledge of the growth mechanism. By aliquots, those particles were systematically analyzed via transmission electron microscopy and fluorescence measurements including quantum yield, blinking and lifetime behavior. Those measurements show direct correlations between nanoparticle diameter and their fluorescence properties. The emission spectras of the different aliquots (left figure) are scaled to quantum yield and show a red shift with nanocrystal size expansion. The right figure shows lifetime values of the starting cores and aliquots.





Giant Dots show very high absorption below 480 nm, high quantum yields and a high photo stability. This makes them ideal for display applications.

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Towards Unidirectional Multi-Electron Transfer Processes in Photocatalysis – A Theory-Driven Design

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Photo-induced electron transfer (PET) processes are the cornerstone of nature's photosynthesis. Understanding of the light-induced processes is essential for the design of novel artificial photocatalysts in the scope of solar energy conversion, e.g. hydrogen generation. Besides the light-harvesting capability of the photosensitizer (PS) the subsequent PET cascades leading either to charge separation (CS) or undesired charge recombination (CR) are of uttermost importance in photocatalysis. Photocatalysts where the PS is bridged by an aromatic ligand, i.e. an electron relay, to the catalytic center are well known for their catalytic activity. However, their performance is often limited due to the population of undesired relaxation pathways associated to degradation or CR.

Here we present a theory-driven design concept to realize unidirectional multi-PET from a PS to the catalytically active site in supramolecular photocatalysts. This is achieved by replacing the commonly used polypyridyl ligands by photoinnocent π-donor ligands, e.g. biimidazolate (bim), Fig. 1a).[1] The PET kinetics are rationalized following a computational protocol recently introduced by our group, Fig. 1b).[2] The comparison of both systems (L=bpy and bim) reveals the highly unidirectional nature of the excited states involved in the initial photoactivation (NIR to UV) as well as the selective quenching of deactivation channels in the modified system.[3]

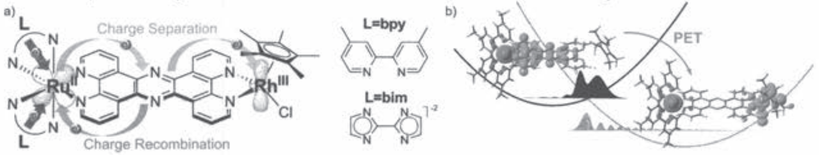

Fig. 1 a) Theory-driven design concept to tune CS vs. CR processes and b) computationally assessed PET kinetics.

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Real-Time Monitoring of Photoinduced Processes on Semiconducting Nanowires in Various Chemical Environments

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Wet-chemically synthesized nanowires are principally utilizable in optoelectronic devices such as solar cells and sensors. However, some aspects of nanowires are not yet fully understood. In particular, nanowires exhibit specific photoluminescence (PL) properties and it is unclear in many respects how the PL of nanowires depends on their chemical environment. Therefore, we performed confocal fluorescence spectroscopy measurements on semiconducting nanowires in flow channels that allow for the controlled exchange of the either gaseous or liquid environment. The measurements were conducted on CdSe and CdS quantum nanowires with diameters of 7.7 nm and 13 nm, synthesized by a solution-liquid-solid method.

A process often witnessed for photoluminescent nanomaterials is a photoinduced PL enhancement. By changing the gaseous surroundings of the nanowires, we were able to assign the PL enhancement (factor 2−3) unambiguously to the oxygen content in the environment. The observed process is suspected to result from a decrease in the number of surface-trap sites due to a photoinduced reaction of unpassivated Cd or Se ions on the surface, in which the respective oxide is formed. A blueshift in the emission wavelength supports this hypothesis. Apart from measurements with different gaseous surroundings, experiments with various aqueous solutions have been performed. We were able to observe both PL quenching and PL enhancement processes, while slowly introducing different substances, such as silver or cadmium ions into the environment of the nanowires. Although a clear physical and chemical interpretation of our first data is yet difficult, we have been able to show that our method can be successfully used for real-time monitoring of processes such as doping, ion exchange and surface passivation.

Direct comparison of fluorescence-detected and coherently detected high-order two-dimensional spectroscopy

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Coherent two-dimensional (2D) electronic spectroscopy is now an established technique to investigate ultrafast quantum phenomena. The concept of 2D spectroscopy can be further extended to higher orders of nonlinearity which probe different effects such as biexciton binding energies or exciton–exciton annihilation (EEA). Here we compare the recently developed techniques of fluorescence-detected high-order multidimensional spectroscopy with coherently detected exciton–exciton-interaction two-dimensional (EEI2D) spectroscopy [1, 2]. We use these techniques to measure high-order spectra of a squaraine dimer. While EEI2D spectroscopy can track exciton dynamics and exciton–exciton interactions from femtoseconds up to nanoseconds, ultrafast biexciton dynamics are usually hard to disentangle due to non-resonant solvent response. Fluorescence-detected high-order spectroscopy does not have this limitation and can measure ultrafast exciton–exciton interactions like they are occurring in this squaraine dimer. Additionally, we use the high-order spectra to measure the coupling of higher monomer states to the biexciton state. Our measurements demonstrate the fundamental and practical differences in coherent- and fluorescence-detected multidimensional spectroscopy and how both techniques can be used to obtain information about highly excited states and their dynamics in molecular systems.

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Towards time-resolved study of two-dimensional semiconductor nanomaterials using extreme ultraviolet spectroscopy

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The study of the interaction of light with matter at the electronic timescale is of great importance to understand complex processes. For example, understanding the ultrafast photo-response in two dimensional (2D) semiconductors like 2D transition metal dichalcogenides will open up new applications such as energy-efficient photonic devices [1]. In our lab, we plan on observing correlated carrier dynamics using broadband attosecond XUV pulses and observe transient absorption changes around absorption edges of the materials following optical excitation. The probe pulses will be generated using a high harmonic generation using a few-cycle near-infrared (NIR) pulses. To generate few-cycle pulses, we have compressed a long NIR pulse from a commercial Ti: Sapphire femtosecond laser system (Astrella from Coherent Inc.). We employ a gas-filled hollow-core fiber (HCF) followed by dielectric chirped mirrors [2]. The laser system produces pulses of 35 fs at an energy of 7 mJ with a repetition rate of 1 kHz at 800 nm, out of which 2 mJ of pulse energy are used for HHG. These pulses are coupled into a ~1.5 m long HCF and having an inner diameter of 300 µm. The fiber is maintained under the gas pressure of Neon at 2 bar. As the pulse propagates through the fiber, self-phase modulation occurs due to third-order non-linear interaction with the gas. This process results in broadening of pulse in the spectral domain which depends on the interaction length, pressure, and intensity. The spectrally broadened pulse coming out of this fiber is then collimated and is propagated through a dispersion compensation module of dielectric chirped mirrors consisting of 8 pairs of chirped mirrors providing a negative group delay dispersion (GDD) of -40 fs^2 each. The compressed pulses are characterized using a commercial dispersion scan system (Sphere Ultrafast Photonics). To date, we were able to achieve ~ 3fs at ~1 mJ pulse energy, which is well-suited for broadband XUV generation using HHG but will also enable near-instantaneous photoexcitation of materials.

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Molecular Functionalization of Inorganic Semiconductor Nanostructures

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Inorganic semiconductor nanocrystals have established themselves as extremely potent and versatile materials for many photonic applications: their high extinction coefficients and tuneable (by means of size variation) absorption and emission characteristics render them ideal candidates as light-harvesters for photovoltaics and photocatalysis as well as active material in light-emitting diodes.

We are currently focusing our research on the molecular functionalization of CdSe- and CdS-based nanomaterials. Exchange of ligands at the nanocrystal surface allows, for instance, the transfer of nanocrystals from organic solvents to water. Not only are the ligands changing the colloidal stability of the nanostructures, but also their photoemissive properties, which can be correlated with the ligands' respective binding modes to the nanocrystal surface. Similarly, by embedding the nanostructures into a redox-active solid state matrix (e.g. polydopamine), the electron transfer from as well as to the photoexcited nanocrystals can be studied. Under different environmental conditions, e.g. under different pH values, the properties of the matrix can be tuned, ultimately changing the charge transfer process at hand. Last, coupling a reactive species, such as a catalyst employed in the hydrogen evolution reaction, to the nanocrystal surface may turn the material photocatalytically active. Here, binding studies of the ligands to the surface and electron transfer processes to the catalytic center are at the core of the investigation.

In this respect, the interactions and impact on dynamics and additional induced charge transfer processes are important for the targeted application. These are routinely probed by steady-state and time-resolved absorption and emission spectroscopies from the UV/Vis to the IR range. This allows us to study processes from a sub-picosecond to the nano- or microsecond timescale.

Growth mechanism and electronic properties of tipped nanorods

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In literature one can find a big variety of syntheses for semiconductor nanoparticle heterostructures. Anisotropic structures are of special interest, since they afford opto-electronic processes with a preferred direction. However, the mechanisms involved in the formation of those materials are still not fully understood. In this work we investigated seeded CdSe/CdS nanords with a ME tip (ME@CdSe/CdS, M = Zn, Cd; E = Se, Te). A synthesis from Deutsch *et al.* [1] was adapted by Enders *et al.* [2] leading to regioselective tip growth on nanorods by successive precursor addition.

Investigation of the synthesis lead to the formulation of a mechanism for the tip growth reaction: According to the law of mass action the second precursor added is quickly converted into [ME] monomer units [3]. Further magic size clusters were found as intermediates and serve as a reservoir for the tip material, thus preventing further formation of new particles.

The electronic properties of the tipped rods were investigated intensely by transient absorption spectroscopy. Through this charge separation could be traced back to distortion of the valence band and formation of coulomb pairs across the tip-rod interface [2].

With time resolved spectroscopy new insights would be accessible, especially by relating both parts of the project. The charge carrier dynamics observed on the femto- to nanosecond timescale are directly dependent on the atomic structure of the material. This structure is governed by the reaction mechanism taking place on a microsecond to hour timescale. Hence time resolved spectroscopy gives the opportunity to correlate the observed effect on the electronic structure with its fundamental origins, lying in the formation mechanism of the nano-heterostructure structure.

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Resolving electronic structure systematically by coherent multiple-quantum multidimensional fluorescence spectroscopy

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Multidimensional optical spectroscopy has proven to be a powerful tool for disentangling coherent dynamical information from all kinds of quantum systems. As the complexity of a system rises, this motivates the development of methods that employ higher orders of nonlinearity to obtain further deconvolution of the nonlinear response of the system and enhanced selectivity. However, common multidimensional experiments suffer from a complex apparatus requiring multiple noncollinear beams, posing a technical challenge regarding the maintainability of phase stability among them. It is also difficult to obtain the absolute phase of high-order signals. To circumvent these issues, we developed a rapid pulse-shaper-assisted approach that employs only a single broadband excitation beam and sensitive fluorescence detection [1,2].

Here we demonstrate the capabilities of our experimental implementation. We present phase-cycling protocols that enable us to acquire simultaneously different types of multiple-quantum two-dimensional and three-dimensional spectra in a single scan. These spectra allow us to resolve systematically information about electronic structure up to sixth order in perturbation theory, revealing electronic coupling, nuclear wavepacket dynamics, ultrafast energy transfer, and multiexcitonic interactions. Due to our 1 kHz shot-to-shot scanning implementation, the total acquisition time is on a timescale of a few minutes which enables us to study systems of limited chemical stability, such as the dianion of TIPS-tetraazapentacene [3]. We further demonstrate our technique on colloidal alloyed semiconductor quantum dots, unveiling exciton-specific phonon coupling, charge cooling dynamics, and the binding energies of hot multiexcitonic states.

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N-Doped Nanographene as Ligand in Metal Complexes

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Nitrogen-doped nanographenes with coordination spheres allow the targeted adjustment of the electronic properties of the ligand, as well as the formation of corresponding metal complexes. Due to their extended π system, nanographene architectures are highly interesting ligands for fast, directed electron transfer over relatively large distances.

Preliminary investigations of the photophysical properties of a polypyridyl-ruthenium complex with a directly attached nanographene ligand have been reported by Vos and Draper et al.[1] This already showed an MLCT absorption with λ_{max} = 615 nm, which is shifted bathochromically by 165 nm compared to $[Ru\ (bpy)_3]^{2+}$ in a nanographene-based orbital set whose nature is still unexplored.

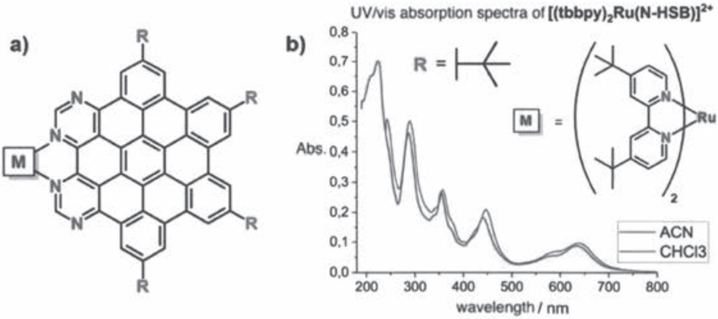

Fig. 1: *a) General structure of the target compound; b) UV/vis absorption spectra of the synthesized Ru complex in different solvents.*

Here, the synthesis and structural characterization of differently substituted precursors of nanographene ligands as well as the targeted introduction of *tert*-butyl groups at the peripheral bipyridine ligands of the Ru center are presented. Initial photophysical studies show an extended bathochromic shift of 19 nm in MLCT absorption, which confirms the potential of the complex for use in photodynamic light therapy.

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Theoretical studies of edge states in transition metal dichalcogenide monolayers and nano-platelet preparation by colloidal synthesis

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Recently, transition metal dichalcogenide (TMDC) monolayers came into focus of several research fields. Especially, MoS_2 is of high interest due to its tunable semiconducting properties. Therefore, MoS_2 potentially can be applied in sensors, nano electronics, catalysis, superconductors, energy harvesting, and other areas.

In this study, two scientific questions were asked, with respect to electronic properties. These are calculated on both geometry optimized structures and on trajectories of molecular dynamic simulations. The theoretical model is density functional based tight-binding [1]. The first question is: Do edges of defects and other limited structures result in similar electronic properties? This was confirmed on triangular defects, triangular nano particles, irregular shaped defects and particles. It was shown, that the electronic properties of these edge containing structures can be interpreted as the sum of edge and bulk properties of two-dimensional MoS_2.

The second question, which has been answered in this study is, how the electronic properties are influenced by the edge termination by sulfur. Calculations showed, that the change of termination doesn't result in significant changes of the electronic properties. In the future, this information could be used to modify TMDC mono- or dual layers to cause interesting optoelectronic properties.

Another interesting TMDC monolayer material is WS_2 which can be synthesized having either conducting or semiconducting properties. In this study, the approach of a colloidal synthesis is demonstrated, which can be modified to receive both modifications. Potentially, the insights gathered by the investigation of WS_2 are useful in the synthesis of other TMDC monolayers like two-dimensional MoS_2 as well.

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Triplet exciton dynamics at silicon-organic interfaces

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With conventional crystalline silicon (c-Si) solar cells approaching their theoretical efficiency limit, large research efforts are currently devoted to addressing their fundamental loss mechanisms. One appealing strategy to reduce losses due to carrier thermalization is the implementation of organic layers that can split the energy of blue photons into two triplet excitons via singlet fission.

We have shown earlier that a layer of the singlet fission-active conjugated organic molecule tetracene (Tc) can be implemented into a c-Si based solar cell without detrimental effects on the device characteristics, but also found very inefficient conversion of the singlet fission-derived triplet excitons into extractable charge. [1] Recently, Einzinger et al. demonstrated that modifying the Tc/c-Si interface with an ultrathin HfON interlayer enhances the triplet exciton energy transfer. [2] This approach represents only one of several possible organic/c-Si interface modification schemes. For example, we exploited electron acceptor molecules to tune the interfacial energy-level alignment. This contribution summarizes the most important interface modification schemes for Si-organic interfaces and the present understanding of the electronic and geometric interface structures. This includes our recent results from near-edge x-ray absorption fine-structure, photoelectron spectroscopy, and density functional theory.

We can resolve the effects of the interface modification schemes on a device level, based on our solar cell platform. However, deriving a mechanistic understanding requires additional time-resolved techniques. The poster presents our current strategy to monitor the excited state dynamics by means of time-resolved photoluminescence and two-photon photoelectron spectroscopy and will hopefully initiate an exchange of ideas in order to identify suitable innovative experimental approaches.

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Time Resolved Photoemission Study of the Charge Transfer Dynamics in Anatase TiO2 for CO Photooxidation to CO2

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Femtosecond X-ray laser pulses coupled with an ultrafast optical laser have been used to directly follow the reaction dynamics of the photooxidation of CO to CO_2 on anatase $TiO_2(101)$ in real time. The photocatalytic reaction is experimentally observed to take place between 1.2 - 2.8 ps via the formation of CO_2, prior to which no intermediate species are observed. The reaction is initiated following the direct transfer of electrons from TiO_2 to adsorbed O_2, made possible by the presence of intragap unoccupied O_2 levels leading to the formation of a charge transfer complex with 770 nm light activation, in line with theoretical calculations. This study highlights the ability of free electron lasers to overcome the challenges faced due to the short lived nature of reaction intermediates, allowing one to investigate photocatalytic reactions in real time and thus to obtain the fundamental knowledge of the underlying mechanisms that is crucial for catalyst optimization.

Investigation of photolabile protection groups as tools for time-resolved structural dynamics

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Photolabile protection groups (PPGs) are compounds, which release a part of their structure upon a light trigger. The leaving group/substrate can trigger subsequent reactions hence the PPGs can be used as a tool. Multiple applications are possible, either in organic synthesis or polymer science to mask certain building blocks until the light trigger is present. Another example for an application is the use of PPGs in serial crystallography for enzymatic reactions. Here, the release of the leaving group sets the time-zero of the whole experiment as the substrate starts to interact with the enzyme. The spatial and temporal control of the release allows a precise management of such experiments. The actual knowledge of the reaction mechanisms of PPGs is necessary to control the subsequent processes as the reaction times and intermediates could interfere with the experimental plan. The investigation can be done by transient absorption spectroscopy (TAS), laser flash photolysis (LFP) or advanced infrared spectroscopies. I investigated compounds of the PPGs para-hydroxyphenacyl and ortho-nitrobenzyl by TAS and LFP successfully and determined some of the reaction intermediates and times. One issue at the investigation of PPGs is the irreversible reaction pattern and loss of signal intensity throughout the measurement. Therefore, a strategy and tools for a fast sample delivery are necessary to maintain signal intensities and a pure sample without the photoreaction products accumulating in the signals.

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Synthesis and bandgap engineering of anisotropic ZnSe/CdS heterostructured colloidal nanoparticles

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Anisotropic colloidal heteronanostructures like dot-in-rod (DR) or tetrapod particles are of great interest because of their tuneable optoelectronic properties. In comparison to the classical CdSe/CdS type-I heterostructures, particles with a ZnSe core and a CdS shell have a type-II band-alignment and thus exhibit delocalized charge carriers after formation of an exciton. This behaviour makes these particles interesting for various application like catalysis.

Here we present the synthesis of type-II ZnSe-core/CdS-shell nanoparticles of different shapes. In a first step, ZnSe cores were synthesized, which were crystallized in the zincblende crystal structure. Depending on the size of these ZnSe cores, in a subsequent CdS-growth step, DRs or tetrapods were obtained. The shell crystallized predominantly in the hexagonal wurtzite structure. They showed fluorescence between 570 nm and 600 nm with quantum yields up to 30 %. Rather long fluorescence lifetimes of up to 250 ns were measured, indicating spatially separated charge carriers of the exciton. When the reaction parameters were changed, the degree of interface alloying could be adjusted by introducing cadmium into the core. A red shift of fluorescence wavelength and shortening of fluorescence lifetime was measured, which depends on the amount of cadmium in the core. This indicates a change of the band alignment, pointing towards the transition from type-II to type-I heterostructured colloidal nanoparticles.

Mixed Semiconductor and Noble Metal Nanoparticle Gel-networks

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Multifunctional nanomaterials are of a great interest in the field of sensing, energy harvesting, and catalysis. Combining the multifunctionality, high surface-to-volume ratio as well as well-defined morphology at the nanoscale makes these nanosystems a more promising candidate for extended field of application. In the recent decade, nanoparticle synthesis provide reliable building blocks with controllable size [1], shape [2] and surface chemistry. Consequently, building up self-assembled structures (*e.g.* gels) from well-designed nanoparticles created a new class of materials, that are of great research interest due to their high volume to mass ratio. The properties of the building blocks can be merged, improved and even extended significantly upon combination of different materials at the nanoscale. For this objective, a multicompound system consisting of interconnected semiconductor and metal nanoparticles (network structures)[3] leads to questions how these two compounds are interacting. Upon illumination, excitons can be generated in the semiconductor parts of the assembled structures. The contact to a metal compound allows the accumulation of the electron in the metal region, while the hole can be trapped in the semiconductor. Based on this charge carrier separation, the system is able to be used for oxidation (hole) and reduction (electron) in an improved manner. In the present work, the above-mentioned system is composed of CdSe/CdS nanorods and noble metal nanoparticles as two different compounds building up the hybrid, multifunctional gel network.

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Separated and recombined again – Tracking ultrafast bimolecular charge transfer in iron-sensitizer based systems

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There have been steady efforts in replacing expensive and scarce metals in photosensitizers by more abundant first-row transition metals. Switching from e.g. ruthenium to iron would make photosensitizers cheaper and thus enhance their chances to be used in wide spread applications.

Using steady-state and time-resolved spectroscopy, we investigated photoinduced bimolecular charge transfer processes involving a novel iron based photosensitizer and sacrificial donors triethylamine (TEA) as well as *N,N*-dimethylaniline (DMA).

The photosensitizer of choice was the *N*-heterocyclic carbene iron based complex (FeNHC) [Fe(phtmeimb)2]+ (with phtmeimb being [phenyl(tris(3-mehtyimidazol-1-ylidene))borate])[1]. The photochemistry involving this FeNCH is in a way particular as it involves unconventional doublet Ligand-to-Metal Charge Transfer (^{2}LMCT) photoactive excited state. To identify the intrinsic dynamics we investigated a broad range of quencher concentrations, omitting the diffusion limit and enabling us to study processes on the ultrafast timescales.

For both donors we do not observe any significant formation of photoproduct. Still, the excited state of the photosensitizer is efficiently quenched with estimated charge-transfer rates of $0.05\ ps^{-1}$ and $1.25\ ps^{-1}$ for TEA and DMA, respectively. The subsequent charge recombination with rates of $\sim 0.2\ ps^{-1}$ for both donors, however, inhibits cage escape and thus photoproduct formation.

Overall, this study highlights the importance of monitoring the ultrafast excited state dynamics in these FeNHC based systems. It underlines their potential for photochemical applications but also reveals challenges that still have to be overcome.

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A Kinetic Insight in the Linear Oriented Assembly and Attachment of Au-Nanoparticles towards 1D Structures

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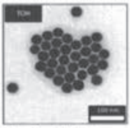

Fig. 1: TEM image of TOHs.

During the last decades, nanoparticles (NPs) have been proven to be great building blocks for constructing new materials with defined structures in 1,2 and 3 dimensions within the nano-, micro- and mesoscale.[1] Prerequisite for targeted synthesis of these structures is a fundamental knowledge about the mechanisms and their kinetics. Here, we present insights in the kinetics of the Oriented Assembly and Attachment of Au-NPs, namely truncated cubeoctahedra Au-NPs (TOHs), towards 1D structures. The monodisperse TOHs were synthesized carrying out a modified synthesis based on a seed-mediated growth method,[2] and characterized applying AUC, TEM (Fig.1) and DLS analytics. The linear assembly of the TOHs is based on a destabilization process due to solvent exchange and explained by dipole induced orientation of the NPs.[3] By analyzing the change in the surface plasmon resonance spectra with time-resolved UV-Vis measurements, the Oriented Assembly of TOHs could be investigated in-situ (Fig. 2). UV-Vis, DLS and AUC analytics suggest a step growth polymerization process for the Oriented Assembly of the TOHs, which was also found for other systems of inorganic NPs.[4] Applying the kinetic laws of step growth polymerization, kinetic insights regarding the formation process of 1D chain-like structures could be gained. By doing so, we resolved and quantified the dependence of the assembly on particle size, temperature, the surfactant (CPC) concentration as well as activation barriers for the following crystallographic fusion of the assembled particles (Oriented Attachment).

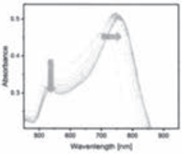

Fig. 2: Investigation of the Oriented Assembly of TOHs by time-resolved UV-Vis.

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Structure-Transport Correlations in Nanocrystal Superlattices

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Mesocrystals are three-dimensional, macroscopic arrays of iso-oriented nanocrystals (NC).[1] Cross-linking the NCs with organic pi-systems facilitates electronic coupling between the NCs and invokes new optoelectronic functionalities.[2] Tailoring these interactions, e.g. by tuning the distance or orientation of the NCs, provides excellent prospects for applications in thermoelectrics, photovoltaics, (magneto-) electronics and optics.[3] This presentation will detail how a combination of wide- and small angle X-ray scattering techniques in conjunction with X-ray cross-correlation analysis can elucidate the full mesocrystal structure of the hybrid superlattices, including the angular correlation with the individual atomic lattices.[4] Simultaneous electric transport measurements allow for a correlation between transport, structure as well as NC orientation, and, ultimately, the revelation of anisotropic transport in such ordered, hybrid materials.

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Excited States of Ru(II) and Cu(I) photosensitizers with dipyrido-phenazine/ naphto-phenanthroline derivates as ligands

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Artificial photosynthesis, such as the light induced reduction of protons to hydrogen, is an increasing field of research over the last years. Photosensitizers with stable long-lived excited states are a key for this process. Therefore, the nature of excited states of Ru(II) and Cu(I) photosensitizers are studied in this contribution.

Complexes with dipyrido-phenazine derivatives as ligands, usually have two excited long-lived triplet states on the ligand. One is located on the dipyrido motif and the other one on the phenazine sphere. The state on the phenazine part is often longer lived, dark and lower in energy than the one on the dipyrido unit.[1]
To get more information on the energy levels and the accessibility of these states, we look at the temperature and solvent dependence of the excited states of Cu(I) and Ru(II) complexes with different substituents at the dppz moiety and related ligands.

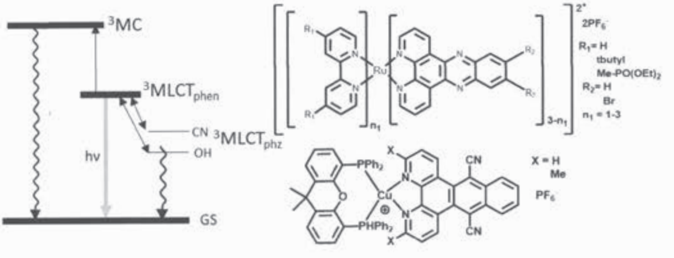

Figure 1. Jablonski Diagram of complexes with with dipyrido-phenazine derivatives as ligands.

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Influence of CdSe Intermediates on Nanocrystal Shape

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During the formation of semiconductor nanocrystals, a class of intermediates has been reported that are called magic-sized clusters (MSC) due to the assumption that they are ultrasmall nanocrystals with defined stoichiometry and shape. These either appear in families that progress from small to large MSCs in a quantised growth before continuous growth of regular nanocrystals takes over. Under different conditions MSCs occur as transient side products that bind nucleation monomer but occur in parallel to regular nanocrystals [1-2]. We have identified a species of MSCs for CdSe and CdS that are characterised by sharp absorption lines at 350 and 309 nm, respectively. Under dry conditions these form 1D fibrils that are connected by phosphonic anhydride bridges and precipitate as a gel [3-4].

At high fibril concentrations further reaction leads to nanorods while at low concentrations it leads to nanodots. The alignment of 1D magic-sized cluster fibrils and its mesostructure has an impact on the resulting nanocrystals. The only way to investigate this is through time-dependent in-situ observation of these changes like in-situ liquid SAXS.

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Proton transport properties of SO^{3-} Groups in Ionic Liquids (IL), studied by Vibrational Spectroscopy

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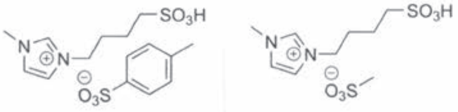
Ionic Liquids (ILs) are very promising materials for future applications, e.g. as fuel cell electrolytes. Using a combination of FTIR and 2D-IR spectroscopy I aim to find the pathway and the mechanism of proton transport between two SO_3^- groups on two different ILs molecules of a new class of proton conducting ILs recently developed. The ionic liquids under study are **IL1**- [BmimSO$_3$H]pTS 1-Methyl-3-(4-sulfobuty)imidazolium para-Toluene-sulfonate and **IL3**- [BmimSO$_3$H]CH$_3$SO$_3$ 1-Methyl-3-(4-sulfobuty)imidazolium methyl-sulfonate. In the figure below are presented the structures of SO3-conducting ionic liquids, synthesized and tested in the research group of Prof. Andreas Taubert, Uni-Potsdam.

Structures of Proton cunducting Ionic Liquids



IL1 - [BmimSO$_3$H]pTS
1-Methyl-3-(4-sulfobutyl)imidazolium
para-Toluene-sulfonate

IL3 - [BmimSO$_3$H]CH$_3$SO$_3$
1-Methyl-3-(4-sulfobutyl)imidazolium
Methyl-sulfonate

The initial studies using FTIR already reveal a clear change in the spectral region of the sulfonate stretch bands between the pure IL and the IL mixed with an additional H$^+$ donor as H_2O or CH_3OH. Currently, further FTIR experiments are performed to investigate how this hydrogen transport is influenced by temperature and different concentrations of the H$^+$ donors. We clearly have seen shifts that occurs in region 1000-1250 cm^{-1}, which is absorption zone of sulfonate group, and strongly indicate that something happens in samples in different H-donor concentration. We have prepared samples with different concentration of water or methanol of ILs and we have obtained FTIR spectrums which have clearly shown spectral shifts in the SO3-spectral region.

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Generating and probing molecular chirality in the gas phase

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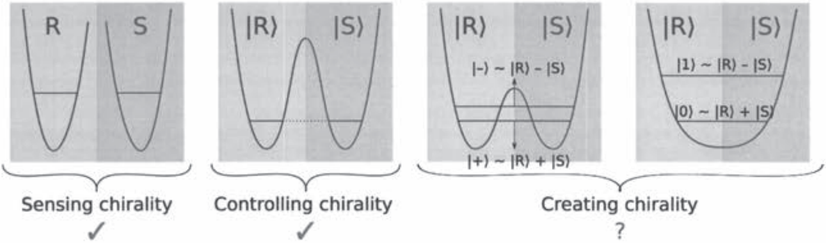
Chirality is an important molecular property.[1-7] For instance, most biomolecules have a certain handiness. Chirality can exist on arious time scales that depend on the barrier separating the enantiomers (see Figure below). Experiments with molecules, which retain the enantiomeric state on timescales longer than the observation time have shown that we can identify and separately control enantiomers.[1-3] However, the case of low or even no barrier separating the enantiomers is either limited to theoretical schemes of coherent control [4–6] or to non-coherent experimental observation of transient chirality.[7]



We present a set of two pump-probe experiments covering the tunneling and barrierless cases of transient chirality. The probe pulse creates a coherent enantiopure wavepacket, which is later probed either by microwave three-wave mixing [1] or by photoelectron circular dichroism [2]. Experimental feasibility is shown by simulating signals for benzyl alcohol and COFCl molecules.

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Roaming Dynamics and Conformational Memory in Photolysis of Formic Acid at 193 nm Using Time-resolved Fourier-transform Infrared Emission Spectroscopy

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In photodissociation of trans-formic acid (HCOOH) at 193 nm, we have observed two molecular channels of $CO + H_2O$ and $CO_2 + H_2$ by using 1 μs-resolved Fourier-transform infrared emission spectroscopy. With the aid of spectral simulation, the CO spectra are rotationally resolved for each vibrational state (v=1-8). Each of the resulting vibrational and rotational population distributions is characteristic of two Boltzmann profiles with different temperatures, originating from either transition state pathway or OH-roaming to form the same $CO + H_2O$ products. The H_2O roaming co-product is also spectrally simulated to understand the interplay with the CO product in the internal energy partitioning. Accordingly, this work has evaluated the internal energy disposal for the CO and H_2O roaming products; especially the vibrational-state dependence of the roaming signature is reported for the first time. Further, given a 1 μs resolution, the temporal dependence of the CO/CO_2 product ratio at v=1 rises from 3 to 10 of study, thereby characterizing the effect of conformational memory and well reconciling with the disputed results reported previously between absorption and emission methods.

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Time-resolved ultrafast spectroscopies performed under tight focusing conditions

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Many time-resolved spectroscopic methods that have been developed to investigate ultrafast dynamic processes in physics, chemistry, materials- and life sciences benefit from the availability of few-cycle femtosecond pulses. In order to exploit both the high temporal resolution alongside with a high spatial resolution, we have developed ultrafast microspectroscopy techniques that provide near-transform-limited, few-cycle femtosecond pulses at the focus of high numerical aperture (NA) objectives commonly used in optical microscopes. Based on this achievement, here, we present the realization of two modalities of time-resolved microspectroscopy that allow studying ultrafast dephasing processes at a diffraction-limited spatial resolution:

First, we demonstrate the measurement of the ultrafast surface-plasmon dephasing time in a single gold nanoparticle, which typically amounts to ~10 fs. By avoiding ensemble averaging over an inhomogeneous sample distribution, our results pave the way for the fundamental study on the relationship between ultrafast surface plasmon dephasing phenomena and the size and shape of an individual plasmonic nanoparticle. Second, we show the experimental extraction of the Raman free induction decay (RFID) constants of vibrational modes in a molecular sample that occupies the minute focus volume of a sub-femtoliter. By implementing both time-resolved and frequency-multiplexed, i.e., two-dimensional, coherent anti-Stokes Raman scattering (2D-CARS) microspectroscopy, where the RFID-constants of all spectrally resolved Raman coherences are simultaneously obtained, ultrafast vibrational dephasing times typically ranging from hundreds of femtoseconds to a few picoseconds are directly time-resolved.

Fluorescence spectral diffusion of single type-II semiconductor ZnSe/CdS dot-in-rod nanostructures at room and cryogenic temperatures

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Previously, we reported on the effect of surface charges on individual type-I CdSe/CdS dot-in-rods (DRs) nanostructures [1,2]. In those systems, photogenerated electrons and holes are both localized in the core. We measured and modelled the diffusion of exciton-fluorescence rates and energies and found that in these DRs, only surface charges near the core region have a significant influence on the optical properties [1].

In this work, we investigate type-II DRs, where the intrinsic band offset leads to a spatial separation of the electron and hole wavefunctions. Here, not only surface charges close to the core region, but also those who are distant from the core should influence the wavefunctions and thus the optical properties due to the dislocation of the electron wavefunction in the shell. Fluorescence measurements at room temperatures of our ZnSe/CdS DRs show a monoexponential decay and an emission energy that can be assigned to an interface recombination between an electron in the shell and a hole in the core. The ensemble fluorescence lifetimes exceeds 100 ns at room temperature. We use confocal fluorescence spectroscopy at cryogenic temperatures and observe abrupt spectral shiftings of the emission line over time, superimposed on smoother spectral diffusion processes. The spectral diffusion covers a larger range in energy than for type-I CdSe/CdS DRs [1], indicating the larger susceptibility of type-II structures to external stimuli, like surface charges. At cryogenic temperatures, we measure shorter fluorescence lifetimes compared to room temperature measurements. We observe a biexponential decay and the fluorescence lifetime-intensity distribution (FLID) suggest stable trion emission at low temperatures. To further analyze the temperature dependency of the charge carrier dynamics, we will use time resolved transient absorption measurements.

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The impact of a fused naphthaloylenebenzene moiety at 1,10-phenanthroline on the electron storage capability and the spectroscopic characterization of the Cu(I) and Ru(II) photosensitizers

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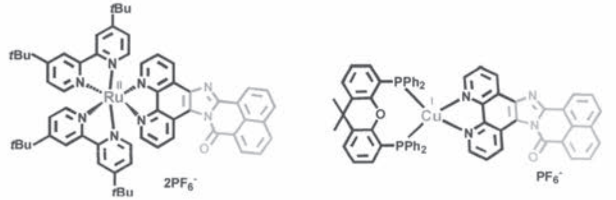
The capture, storage and usage of solar light for light-driven organic reactions or for the production of solar fuels is of increasing importance. This requires the design of efficient and inexpensive photosensitizers for solar energy conversion.[1] In particular, heteroleptic copper(I) complexes are a promising alternative towards traditional photosensitizers based on precious metals and are a main subject of our current research.[1-5] However, these Cu(I) complexes should also possess a strong absorption in the visible, long excited state lifetimes, a reversible electrochemical behavior and a sufficient stability. Moreover, for some applications photosensitizers that are able to store multiple charges are desired. [5]

The integration of an extra electron storage unit in the backbone of the diimine ligand is a possibility to design Cu(I) complexes that allow to store an additional electron. For this purpose, we decided to directly fuse a 1,10-phenanthroline building block with 1,8-naphthalimide. After successful ligand synthesis also the related Ru(II) photosensitizers were made for comparison. Following, a combination of several spectroscopic and analytical methods was used to investigate the structural, electrochemical and photophysical properties of the resulting photosensitizers.

Design of advanced Photosensitizers with additional electron storage moiety



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Temporal Development of a Laser-Induced Helium Nanoplasma

Measured through Auger Emission and Above-Threshold Ionization

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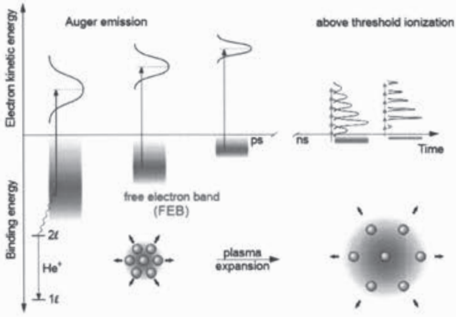
Femtosecond pump-probe electron and ion spectroscopy is applied to study the development of a helium nanoplasma up to the nanosecond timescale. Quasi-free electrons, bound by the deep confining mean field potential, are elevated towards the vacuum level in the nanoplasma expansion [1]. Subsequent electron recombination gives rise to transitions between He^+ states, resulting in autoionization [2]. A time-resolved analysis of the energy transfer to quasi-free electrons reveals a transient depletion of the Auger recombination and allows for a temporal gate to map the distribution of delocalized electrons in the developing mean field. Furthermore, we introduce transient above-threshold ionization as a diagnostic tool to trace the recombination of delocalized electrons near the vacuum-level into highly excited Rydberg states.



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N_2^+-lasing Induced by Filamentation in Air for Femtosecond Coherent Anti-Stokes Raman Spectroscopy

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Filamentation induced by high-power ultrashort laser pulses in air originates from a dynamic balance between self-focusing of Kerr effect and defocusing of the plasma generation, which could propagate over extended distances much larger than the typical diffraction length [1,2]. Odhner et al. [3] reported on the coherent anti-Stokes Raman scattering (CARS) signal of different gases making use of the spectral broadening accompanied by filamentation in air. The 2nd harmonic of the 800 nm beam was used as a probe. In remote sensing applications the temporal and/or spatial alignment between the pump and probe beam is hard to achieve, e.g. in large scale industrial facilities. On the other hand, the laser-like emission of the excited N_2^+-ions accompanied by filamentation has attracted much attention in recent years [4, 5].

We investigate both ultrashort pulse filamentation and lasing action of N_2^+ for pump-probe experiments. The N_2^+ lasing peak at ~391 nm $(B^2 \sum_u^+, v''=0 \rightarrow X^2 \sum_g^+, v'=0)$ may indeed act as the probe pulse for CARS in air. In order to generate a ro-vibrational fs-CARS signal of air, the white-light continuum has to cover the Raman shift of N_2 and O_2. Then, the lasing pulse at ~391 nm probes this Raman excitation, resulting in a fs-CARS peak. In this study, the CARS signals of N_2 and O_2 in air were detected.

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